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# Initiation and Sensitization of Detonable Hydrocarbon/Air Mixtures for Pulse Detonation Engines

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FINAL REPORT

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## Executive Summary

The initiation of detonation in hydrocarbon fuel-air mixtures and the effect initiation has on performance are two key issues for the assessment and progress of Pulse Detonation Engines. This report presents the results of experimental studies into the initiation of detonation and the impact of initiation on the impulse generated in a single-cycle Pulse Detonation Engine. In order to facilitate the prompt initiation of detonation, a number of chemical sensitizers were considered (nitrates, nitrogen dioxide, peroxides). None of these were shown to have a significant sensitizing effect, as quantified either by the run-up distance to detonation or by the detonation cell size. Partial reforming of the fuel/oxygen mixture via the "cool flame" process was shown to have a significant sensitizing effect, reducing run-up distance by a factor of two and cell size by a factor of three. This effect was transient, in that it was only observed immediately prior to the onset of cool flame. The ability to initiate an unsensitized fuel-air mixture via a turbulent jet of combustion products was demonstrated in two different facilities at different scales. Different techniques of creating a nearly instantaneous constant volume explosion in a precombustion chamber were investigated. These techniques were then used to drive a turbulent jet of combustion products through orifices of different geometries. The use of flame tubes was shown to be highly effective in creating constant volume explosion pressures, and the use of an annular orifice to create a centrally focused jet was found to be the most effective orifice design. The scaling for jet initiation of detonation was determined in terms of the mixture characteristic cell size.

The role of initiation in the impulse generated by a single cycle of a Pulse Detonation Engine was also investigated using a ballistic pendulum. It was shown that, over a wide range of equivalence ratios, the impulse generated by direct initiation of detonation was the same as that generated by deflagration to detonation transition. Initiation at the open *vs.* closed end of the tube was also shown to give comparable impulse. The friction and heat losses to the tube were shown to have a significant effect on impulse, which become dominant as the tube aspect ratio (length to diameter ratio) increased to large values.

The results of this study did not identify a chemical additive that is a significant sensitizer to detonation. Reforming the fuel via cool flame was shown to have a significant effect, but how this technique would be implemented in an engine remains unresolved. An intense jet of combustion products is capable of initiating detonation in a fuel/air mixture, provided the jet diameter is sufficiently large. The impulse measurement results show that initiation of detonation may not be necessary if the combustible mixture can still be burned quickly enough via fast turbulent flame. The effect of heat transfer and friction must be carefully considered in interpreting impulse measurement.

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# 1. Introduction

The evaluation and development of the Pulse Detonation Engine (PDE) concept requires a number of fundamental issues in detonation science to be addressed. In particular, the ability to initiate relatively insensitive fuel/air mixtures promptly and within the length scales of an engine is a key problem. Most fuel-air mixtures at atmospheric pressure have a minimum diameter of detonation propagation on the order of 5 cm, similar to the dimension of proposed engines. The makes establishing a detonation within the engine dimensions and the cycle timescales challenging. This first effort this program addressed was exploring techniques and phenomenon that may permit a more rapid initiation of fuel-air detonations in tubes (see section "Initiation and Sensitization" below).

The other issue is the effect of detonation initiation on the impulse (integrated thrust) generated. In particular, the consequences of the mode of initiation (direct *vs.* DDT) and the mode of propagation (CJ detonation *vs.* fast turbulent flame) on PDE performance had not previously been established. Thus, the second topic addressed in this effort was to determine the effect of initiation on the impulse of a PDE (see section "Impulse" below). This effort also necessitated developing techniques to measure impulse and quantifying the other factors that influence impulse, such as friction and heat transfer.

The key results of these studies are summarized below; details can be obtained from the referenced publications, which are reproduced here as Appendices 1-9.

# 2. Initiation and Sensitization

## 2.1 Role of Igniter

A common assumption in the development of PDE's is the necessity of using a powerful igniter. Unless an igniter is powerful enough to directly initiate detonation (requiring ~100-1000 kJ for fuel/air mixtures), the flame ignited must still undergo a process of deflagration to detonation transition (DDT). This process occurs largely independent of the particular igniter used. It is possible that, if a very powerful spark is used, a more rapid transition from a laminar to a turbulent flame may occur, which in turn may shorten the time required for DDT. The length scale of the transition to detonation (run-up distance) is largely independent of the igniter. This fact was demonstrated in mixtures of propane/oxygen/nitrogen in an obstacle-laden 15-cm-diameter tube by using a weak spark in comparison to the same spark, confined in a small pre-combustion chamber. The intense jet of combustion products emerging from the precombustion chamber resulted in a reduction of approximately 50% of the time required for DDT. The length required for DDT was unchanged, however. This is due to the fact that the majority of time for DDT is consumed by the early laminar to turbulent flame transition, while the length scale is dominated by the acceleration of the turbulent flame to velocities where shock-generated conditions permit the final onset of detonation. It is possible that an intense jet of combustion products can result in the direct initiation of detonation, as demonstrated in the next section (see "Jet Initiation" below). Jet initiation, however, requires a large diameter jet driven by a precombustion chamber which is similar in cross-sectional area to the main detonation tube itself in the case of a PDE, and the jet's ability to initiate detonation is decoupled from the ignition source.

This study clearly demonstrated that the role of obstacles play a much more significant role in governing the run-up distance to the onset of detonation than does the power of the igniter.[1]

## 2.2 Jet Initiation

The ability of an intense, turbulent jet of combustion products to initiate detonation via rapid mixing has been well established in the detonation literature for more than 20 years. Most of these studies used either long flame acceleration tubes or detonations to drive the turbulent jet of products. In this study, the ability to create the conditions necessary for jet initiation of detonation by using a small volume precombustion chamber (≈ one-two tube diameters long) was explored.

In order to create a near constant volume explosion to drive the jet of combustion products, it was necessary to investigate techniques to burn out a volume of gas in less than the characteristic acoustic time of the precombustion chamber (~1 millisecond). A variety of techniques were examined: single spark, array of sparks, flame jet, and combinations of flame jets. Any technique using a spark for ignition of the mixture required on the order of 10's to 100 msec for burn-out of hydrocarbon fuel-air mixtures. The use of multiple flame jets was able to burn out the entire volume in millisecond timescales. The use of multiple jets, however, lowered the peak pressure reached in the precombustion chamber to approximately half of the ideal, adiabatic constant volume explosion pressure. This was attributed to the heat losses to the greatly increased surface area of the flame tubes. Thus, it appears there is an optimal combination of flame tubes to generate an effectively instantaneous burn out of a volume of gas and to reach peak pressures.

The precombustion chamber was used to drive a turbulent flame jet through an orifice plate. A variety of orifice plate geometries were investigated: single hole, multiple hole, annular slot, and centrally-focused annular slot. The mixture sensitivity was controlled by varying the nitrogen dilution in a propane/oxygen/nitrogen mixture, and the critical mixture sensitivity for a given precombustor/orifice plate combination was determined. The results indicate that the annular orifice plate (with or without ring to focus jet inward) appeared to be most effective in initiating detonation. The technique used to burn-out the prechamber did not have a significant effect if the annular orifice plate was used, provided that near constant volume combustion pressure was reached (for other orifice plates, the more rapid burn out techniques did appear to be more effective).

These tests were initially done in a 6.5-cm-diameter detonation tube, and the results were scaled to a 15-cm-diameter tube, again using propane/oxygen/nitrogen mixtures. The results were successfully scaled with the detonation cell size: the critical diameter of jet required in the optimal case was 4-5 times the characteristic cell size of the mixture.[2]

## 2.3 Sensitization

### 2.3.1 Nitrates

The use of nitrates as sensitizers has been considered in the past, as motivated by their use as ignition improving agents in diesel fuel. In this study, experiments with 2-ethylhexyl nitrate were performed at room temperature in propane/oxygen/nitrogen mixtures. The results were inconclusive; the effect on run-up distance to detonation was not larger than one or two tube diameters. The effect was difficult to isolate due to the low vapor pressure of 2-ehn, which made it difficult to introduce into the mixture, and difficult to evacuate the residual liquid afterwards. This difficulty motivated using gaseous $NO_2$ instead.

### 2.3.2 $NO_2$

The proposed mechanism of nitrate sensitization is via decomposition into $NO_2$. Thus, to determine if a sensitizing effect is possible, experiments with direct $NO_2$ addition to propane/oxygen/nitrogen mixtures at atmospheric conditions were carried out. A 14.5-cm-diameter detonation tube with obstacles was used. Considerable care was taken in selecting the composition of the mixture to ensure that the $NO_2$ would not affect the overall energetics of mixture.

The results of these tests showed that $NO_2$ had a negligible effect on mixture sensitivity, as quantified by either run up distance or cell size. This suggests that nitrates are not likely a viable sensitizer for hydrocarbon fuels.[3]

### 2.3.3 Peroxide

The use of peroxides as sensitizers was also considered. The use of peroxides as sensitizer was motivated by the results obtained with cool flame partial oxidation (see next section). Chemical kinetic studies suggest that peroxides may be responsible for the observed increase in sensitivity observed with cool flames.

The peroxides considered were tert-butyl hydroperoxide (tbhp) and hydrogen peroxide (50% solution in water). The fuel used was decane with oxygen at low pressure (7-9 kPa) in a 5 cm diameter heated detonation tube. The tube was heated in order to ensure the vapor pressures of the fuel and peroxide were sufficient to maintain a gaseous mixture. The mixture sensitivity was quantified by the run-up distance to detonation and measurements of cell size. The concentration of peroxides was varied over up to 60% of the fuel in the case of tbhp and up to 30% of the fuel for hydrogen peroxide solution

No significant sensitizing effect was observed with either tert-butyl hydroperoxide or hydrogen peroxide, either in terms of run-up distance to detonation or cell size. The presence of tbhp did result in a shift in mixture sensitivity to fuel-rich conditions.[4]

### 2.3.4 Cool Flame

The sensitizing effect of cool flame partial oxidation on hydrocarbon fuels was first identified by Shchelkin and Sokolik in the 1930's. As this effect is the only known significant way to re-form a fuel/oxygen mixture into a significantly more sensitive

mixture, it was decided that verifying this effect was of importance and its further investigation may indicate promising techniques to sensitize fuels for PDE applications.

These tests used pentane/oxygen mixtures at low pressures (25 kPa). The tube temperature was varied over a range 50 to 400 °C in order to see the effect of cool flame (cool flame onset temperature ≈ 250 °C). It was also essential to control the exact sequence of injection and ignition, since in the cool flame regime, the mixture composition varies with time.

The results reproduced the Shchelkin and Sokolik sensitization effect by showing a 50% reduction in run up distance to detonation if the mixture was ignited immediately prior to the onset of cool flame. A reduction in cell size to approximately one third of its pre-cool flame value was also observed. If the mixture was ignited after the appearance of cool flame, a decrease in mixture sensitivity was observed, as noted by an increase in both run up distance and cell size.

Chemical kinetic simulations of the cool flame processes, followed by simulations of the ZND reaction zone length, also showed the sensitizing effect of cool flame. These chemical kinetic studies also attempted to identify the particular specie or mechanism responsible for the observed effect. A series of calculations in which different parameters (specie concentrations, temperature, etc.) failed to identify a single factor that was responsible for the observed effect. Thus, it appears that a combination of temperature, peroxides, and free radicals which appear during the cool flame process is responsible for the observed effect.[5,6]

# 3. Impulse

## 3.1 Effect of Initiation: Direct vs. DDT

In order to measure the net impulse (integrated thrust) of a single detonation cycle, a ballistic pendulum technique was developed. An open-ended detonation tube was suspended from wires, and the recoil of the tube was measured upon detonation. Apparatus-dependant factors in the experiment (length of wires, diaphragm spanning open end, etc.) where shown to have a negligible effect on the impulse.

Tests were done with both direct initiation (via large capacitive discharge) and deflagration to detonation transition (via weak spark at closed end). Both were shown to generate the same impulse over a wide range of equivalence ratio for hydrogen-oxygen mixtures. Only at very rich and very lean fuel equivalence ratios, in which DDT was not completed by the time the combustion wave reached the end of the tube, was a deficit in thrust observed for the case of DDT. The case of initiation at the open end of the tube was also investigated. Again, no difference was observed in direct initiation *vs.* DDT at the open end. A slightly lower impulse (approximately 15% lower) was consistently obtained for initiation at the open end in comparison to initiation at the closed end for the same mixture. This difference is comparable to the experimental scatter.[7]

### 3.2 Effect of Heat Transfer and Friction

Comparing the results of this study with those obtained at other facilities showed a consistent offset in the impulse obtained for propane/oxygen mixtures. This effect was further investigated by varying the aspect ratio of the detonation tube used. It was found that the impulse decreased as aspect ratio (*L/D*) increased. A simple analytic model for friction and heat transfer on the internal tube wall was able to reproduce this effect.[8]

## 4. Conclusions

To date, no viable means to chemically sensitize a hydrocarbon fuel/air mixture has been identified. While the "cool flame" partial oxidation process does result in a mixture with greatly enhanced sensitivity to detonation, this effect has not been reproduced by using additives of peroxides, nitrates, or nitrogen dioxide. This suggests that only the presence of nonequilibrium species (free radicals) in the cool flame is responsible for the observed effect. This result has paralleled the conclusions of other researchers during this same period; no sensitizing chemical additive has been found.

The ability of a jet of combustion products originating from a precombustion chamber to initiate detonation has been established. The results of this study indicate that the diameter of jet must be approximately 4 to 5 times the characteristic cell size of the mixture to be initiated. This volume of gas can be effectively burned-out in millisecond timescales by using multiple ignition points and flame jets. The use of annular, centrally-focusing orifice plates appears to be the most promising geometry for detonation initiation via a jet of combustion products.

The results of the impulse study strongly indicate that the impulse generated by a single cycle of a PDE is only a function of the chemical energy stored in the tube. The impulse is independent of the details of the combustion initiation process (direct initiation *vs.* DDT), provided all of the gas burns without being spilled from the open end of the tube. The effect of tube length has been correlated to heat and friction losses to the walls of the tube, with heat losses probably accounting for the dominant effect. This effect clearly shows up as a reduction in specific impulse for very large aspect ratio (*L/D*) tubes. It is likely that this will only be a higher order effect in the length of tubes used in actual PDE's. Heat losses may also explain the small difference observed between detonation initiation at the open vs. closed end of the tube.

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# Appendix 1: Sensitization of Fuel-Air Mixtures for Deflagration to Detonation Transition

**Reprint of:** Higgins, A.J., Pinard, P., Yoshinaka, A., and Lee, J.H.S., "Sensitization of Fuel-Air Mixtures for Deflagration to Detonation Transition," *High-Speed Deflagration and Detonation: Fundamentals and Control,* Elex-KM Publishers, Moscow, Russia, 2001, pp. 45-62.

# SENSITIZATION OF FUEL–AIR MIXTURES FOR DEFLAGRATION-TO-DETONATION TRANSITION

**A. J. Higgins, P. Pinard, A. C. Yoshinaka, and J. H. S. Lee**

The mechanisms responsible for the acceleration of a laminar flame to a self-sustained detonation are discussed, and means to influence (either accelerate or retard) each mechanism are identified. The role of the igniter is to establish a laminar flame. While a very powerful igniter may be able to bypass the laminar to turbulent flame transition process, it has little influence on the run-up distance to detonation, since the turbulent flame must still accelerate to velocities on the order of 1000 m/s before the onset of detonation can occur. Only a very large diameter (on the order of the critical tube diameter) flame jet may be able to bypass the turbulent flame acceleration process and directly initiate detonation. Usually, obstacles are used to effect a rapid acceleration of the turbulent flame. The greater intensity of turbulence and transverse shock waves created by obstacles permits a wide spectrum of turbulent flame velocities to be observed. In the final onset of detonation, the mixture sensitivity (as determined by chemical kinetic rates) is the dominant factor governing initiation. A number of possible sensitizing agents (acetylene, $NO_2$, various nitrates) are considered, but thus far, only the "cool flame" processing of hydrocarbon–air mixtures appears to have a significant effect in reducing the length scales required for initiation of detonation.

## 1 INTRODUCTION

Deflagration-to-detonation transition (DDT) is the process by which an initially laminar flame undergoes a sequence of changes in propagation mechanism, ultimately resulting in a self-sustained supersonic detonation. While DDT is typically thought of as an acceleration process (since the combustion wave velocity can span four orders of magnitude), it is more properly considered as a process

of altering the mechanism of wave propagation, with the propagation velocity reflecting the rate at which different mechanisms occur. Appreciating when these different mechanisms are at work lays a foundation for understanding and ultimately controlling DDT.

The initial stages of flame kernel formation and growth as a laminar flame are dominated by diffusion of heat and radicals to the unburned layer ahead of the flame. A whole host of natural instability mechanisms (e.g., Rayleigh–Taylor, Landau–Darrieus, Markstein, etc.) act to wrinkle the flame and increase the burning rate per unit volume and, consequently, increase the propagation velocity.

A more significant role is played by the flow created ahead of the flame due to volumetric dilatation of the combustion products: in a confined geometry (i.e., a pipe), this flow becomes turbulent and a flame propagating into a turbulent flow field undergoes a dramatic increase in the burning rate. This transition to turbulence also sets the stage for feedback between the flow ahead of the flame and the flame itself. The feedback can occur via a fluid dynamic mechanism, whereby an increase in burning rate increases the flow velocity of the gas ahead of the flame, thus amplifying the intensity of turbulent flow into which the flame propagates. The unsteady flow ahead of the turbulent flame also allows for a gasdynamic feedback mechanism, provided the unsteady compression waves sent ahead of the flame increase the temperature sufficiently to produce an accelerating effect on the reaction rates. A discussion of the relative significance of these various instability and feedback mechanisms can be found in [1, 2].

Regardless of the particular mechanism, when the combustion wave reaches very high turbulent flame speeds (600–1000 m/s), it clearly becomes a mixing limited, rather than a diffusion controlled, process. The fact that high-velocity turbulent flames propagate with mixing rates apparently greater than those required to quench the flame remains one of the unresolved issues in this poorly understood regime of combustion [2].

When the turbulent flame reaches velocities ($\sim$ 1000 m/s) where the compression waves pushed ahead of the flame coalesce into a shock generating sufficient adiabatic compression to initiate chemical reactions, the conditions for the final onset of detonation may be present. The final initiation of detonation is usually associated with the abrupt appearance of explosion centers or "hot spots" in the shock – turbulent flame complex (the so-called "explosion in the explosion") which rapidly accelerate in the shocked gas to merge with the initial shock.

Moen *et al.* [3] have also identified another mode of DDT due to the progressive amplification of pressure waves traversing the reaction zone at the final stages of initiation. It appears that the onset of detonation invariably involves a rapid wave amplification process. The result of this amplification process is an initially overdriven detonation, often with wave speeds exceeding the steady Chapman–Jouguet (CJ) wave speed by 50–100%, which quickly decays to





a steadily propagating detonation. The sequence of events outlined here is shown schematically in Fig. 1.

Note the presence of obstacles in Fig. 1; obstacles are present in all of the DDT experiments presented in this paper. While DDT does occur in tubes without obstacles, the run-up distance to detonation can be an order of magnitude larger and significantly more stochastic, due to increased sensitivity to the tube wall roughness, position of the igniter, etc. By using a series of regularly spaced obstacles, the tube wall roughness is dominated by the obstacles and hence the results become largely independent of the other details of the apparatus. Extensive prior research at McGill University [4, 5] have identified an obstacle blockage ratio of $\sim$ 40% and an obstacle spacing of roughly one tube diameter as being near the point of diminishing return in obstacle spacing and blockage. Thus, the results obtained with these obstacles are believed to be the near minimum length scales required for DDT, and further optimization of the obstacles would result in only minor changes in the length required for detonation formation.

Due to the abrupt appearance of detonation at the final stage of the flame acceleration process, initiation is traditionally considered as a unique and well-defined event. Recent research on quasi-detonation [6], however, suggests that in tubes with obstacles, the same mechanisms responsible for DDT (local explosion centers resulting from shock interactions with obstacles) may also permit steady propagation velocities as low as one half of the CJ velocity. Thus, a CJ detonation is merely the limiting case of a continuous spectrum of combustion wave velocities, and the division between detonation and highly turbulent flame becomes indistinct. If a combustion wave is "denied" the mechanisms of detonative combustion, either by using a tube smaller than the characteristic cell size of the mixture or by using a tube with acoustic absorbing walls to dampen out cellular structure, then the wave will propagate at speeds of the order of one half the CJ detonation velocity [7, 8].

Recent attention has been focused on the DDT problem as a result of renewed interest in pulsed detonation engines (PDE). The requirement of detonating fuels of practical interest for aerospace and defense applications (Jet A, JP-10, etc.) within the limited dimensions of an engine has stimulated research into schemes by which detonation can be promptly initiated in these mixtures without having to use a predetonator of gaseous fuel–oxygen mixture. Direct initiation (i.e., near-instantaneous deposition of energy into the gaseous mixture, generating a blast wave of sufficient strength and intensity to decay to a self-sustained detonation) would require charges on the order of $\sim$ 100 g of high explosive for each cycle of initiation. Other initiation sources (sparks, lasers, etc.) cannot easily provide this amount of energy ($\sim$ 100–1000 kJ) on a cyclic basis. This leaves "self-initiation," or initiation using the chemical energy of the explosive medium itself, to create the conditions necessary for the onset of detonation.

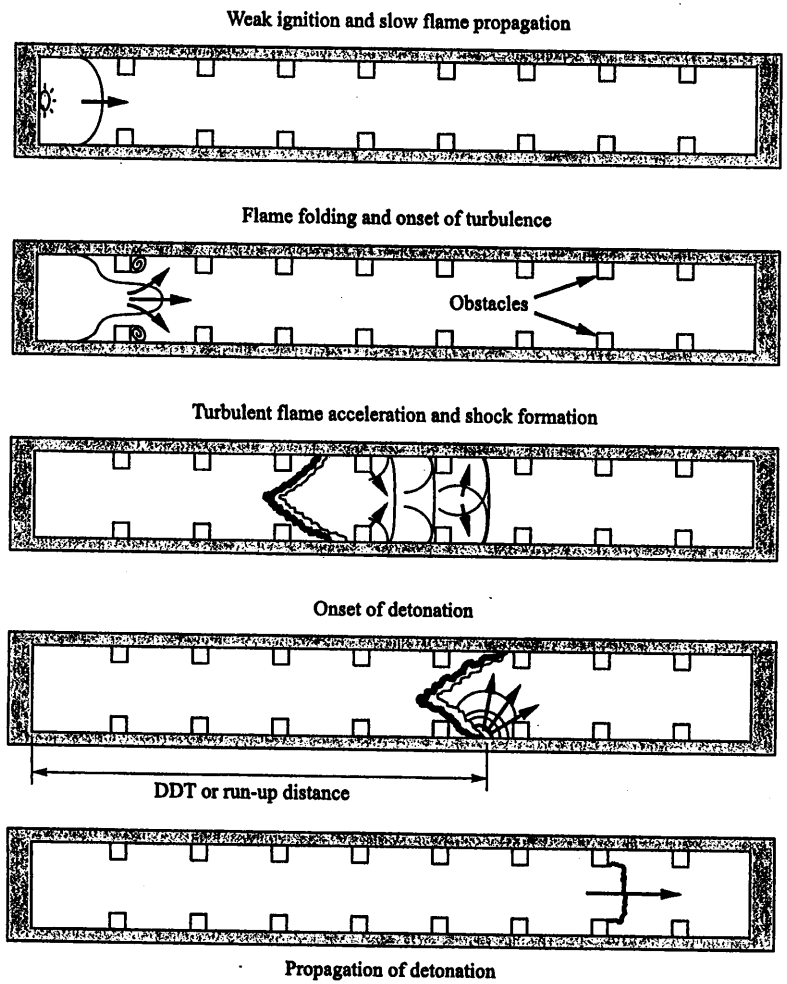


**Figure 1** Schematic illustrating the sequence of events for DDT in tube with obstacles





The most recent estimates of the critical kernel size for planar initiation [9, 10] suggest that the chemical energy available within one to two cell lengths of the explosive mixture is sufficient to initiate detonation in that mixture. The usual path of self-initiation, however, is DDT, and this typically requires an order of magnitude longer length scale before the onset of detonation occurs. For a higher hydrocarbon fuel in air (where the detonation cell size $\lambda \approx 5$ cm), the tube diameter must be greater than $\lambda$ for self-sustained propagation, and typically 10 tube diameters or more are required for DDT. Thus, for hydrocarbon–air mixtures, the length required for DDT approaches or even exceeds the length scales of interest for PDE applications. The fact that, in principle, there exists sufficient chemical energy in the mixture to undergo self-initiation within one or two tube diameters suggests that a significant reduction in initiation length scales could be realized if the appropriate route to detonative combustion can be identified. Knowledge of the mechanisms responsible for DDT and the transition between those different mechanisms is not sufficient at present to identify a "soft" initiation scheme that uses the weak igniter of DDT yet initiates on the short length scales of direct initiation. Experiments with turbulent jet initiation (discussed in Section 2 below) suggest a direction that may prove fruitful.

This paper discusses the authors' current views on mechanisms responsible for DDT and some of the techniques to accelerate or bypass those mechanisms, using recent results from detonation research at McGill University to highlight certain points. This paper is not a comprehensive review, but rather suggests a course of action as to how best attack the DDT problem for PDE applications.

## 2 LAMINAR TO TURBULENT FLAME TRANSITION: ROLE OF INITIATOR

The role of an igniter in DDT is to create an initial flame kernel that will grow as a laminar flame. In confined tubes with ignition occurring at a closed end, the laminar flame will quickly become turbulent due to the various instability mechanisms discussed in the Introduction. Since, for a fuel–air mixture, the laminar flame propagates at speeds of 30–50 cm/s, the time required for the flame to reach the tube wall and make the transition to a turbulent flame can comprise the majority of the time required for the entire DDT process. If a sufficiently powerful igniter is used, it may be possible to bypass the laminar to turbulent flame transition process entirely.

This is illustrated in Fig. 2*a*, where DDT in a propane–oxygen–nitrogen mixture at 1 bar initial pressure occurs in a 15-centimeter-diameter, 2.2-meter

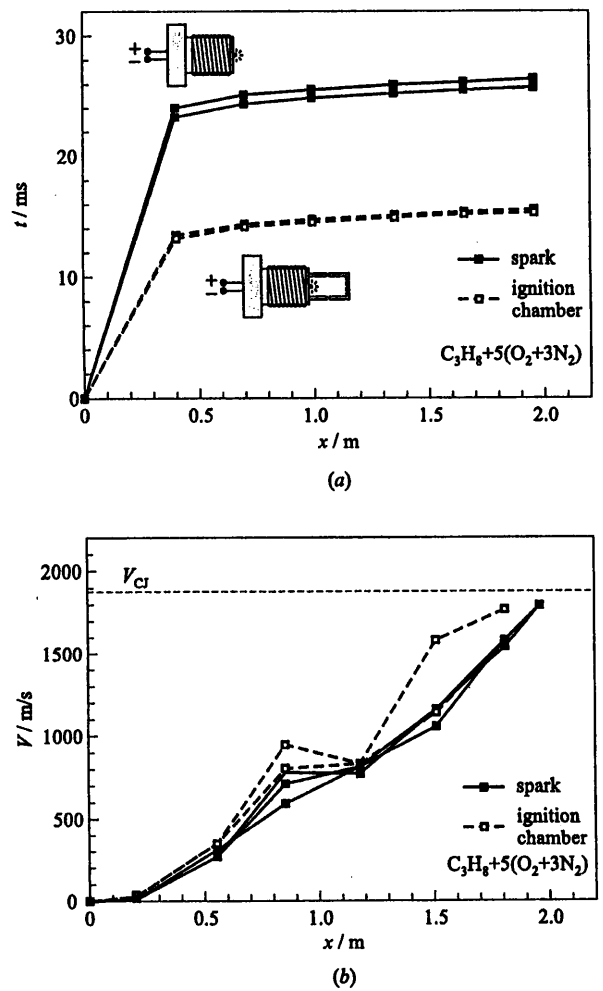


**Figure 2** Distance vs. time (*a*) and velocity vs. distance (*b*) data for a propane–oxygen–nitrogen mixture undergoing DDT in a 15-centimeter-diameter tube with regularly spaced obstacles, as measured by ionization probes on the tube wall. Two different igniters (spark plug and flame jet from precombustion chamber) are shown (initial pressure 1 bar)





long tube. If the typical spark plug igniter is replaced with a small precombustion chamber in which the combustion products jet outward, the time required for DDT is reduced by a factor of more than two (see $x$–$t$ diagram, Fig. 2*a*).

Viewed as a velocity–distance ($V$–$x$) diagram (Fig. 2*b*), however, the results obtained with the two different igniters are indistinguishable. This is because, while the ignition chamber succeeds in creating a turbulent flame earlier, the turbulent flame must still propagate the same distance before reaching velocities sufficient for the onset of detonative combustion. This result is in sharp contrast to the often-repeated statement found in the PDE-related literature: that a powerful igniter is necessary for short DDT. While the laminar to turbulent flame transition comprises the majority of the time required for DDT, it is negligible in the length scale required for DDT.

While it may be argued that a very powerful igniter, or array of igniters, may be capable of near-direct initiation of detonation, studies of detonation initiation by turbulent flames emerging from obstacle-laden tubes [11] and packed beds of porous media [12] suggest that turbulent flame velocities in the 700–1000 m/s range are necessary for detonation initiation, with turbulent fluctuating velocities on the order of the sonic speed. This would necessitate an initiator of sonic or supersonic jets of hot gas (probably combustion products) over the entire tube area. Such an initiator would likely consist of a volume of combustible gas that must itself undergo transition to turbulent flame propagation anyway. Even if such an initiator can be realized, the length scale required for further acceleration and transition to detonation is still very large (approximately 1 m in Fig. 2). Thus, a powerful igniter can play an important role in rapid initiation techniques, but only as a means of initially creating a highly turbulent flame. The acceleration of that flame to detonation still consumes a considerable distance.

In the limit of a large diameter jet of combustion products, direct initiation of detonation is possible and has been demonstrated in unconfined environments for a variety of different experimental set ups [13–18]. These experiments usually involved using a precombustion chamber in which a highly turbulent flame was developed and then allowed to expand into the main chamber via an abrupt expansion or by passage through an orifice plate. Thus, these experiments are more properly thought of as separating the turbulent flame acceleration process from the final onset of detonation by a diaphragm or orifice plate. The jet diameter in these experiments needed to be much greater (typically a factor of 5 greater) than the critical tube diameter ($d_c = 13\lambda$) for successful initiation. Jet diameters of 40–100$\lambda$ were often required, thus making this type of initiation too large to be applied directly to PDE.

Results [15] and the more recent experiments [19], however, suggest that turbulent flames may be capable of direct initiation upon emerging from a tube diameter smaller than the critical diameter for detonation transmission. In addition, the effect of tube confinement on this mode of initiation has not been

investigated and may permit direct initiation by turbulent flame jets to be realized in the length scales of interest to PDE's.

## 3 HIGH-SPEED TURBULENT FLAME ACCELERATION: ROLE OF OBSTACLES

Starting with the work of Laffite [20] and Chapman and Wheeler [21] in the 1920's, the role of obstacles and tube wall roughness on turbulent flame acceleration has been extensively studied and reported [4, 5, 22]. The current picture of the role of obstacles is to intensify the turbulent shear mixing by creating both vortices in the wake of the obstacles and transverse shock waves. Obstacles thus permit orders of magnitude reduction in the length scale required for DDT, and their presence allows turbulent flames to propagate at steady velocities of 1000 m/s, as opposed to the 100 m/s typically observed in smooth-walled tubes. The high intensity of turbulent mixing induced by obstacles and the hot spot formation mechanisms such as Mach reflections occurring off obstacles allows high-speed turbulent flames to mimic cellular detonative combustion and thus propagate at very high speeds. This blurring of distinction between detonations and very high-speed turbulent flames gives rise to the term "quasi-detonation."

The ability of obstacles to promote very high-speed turbulent flames is well illustrated in the results of Chao *et al.* [23], in which a 30 × 30 cm tube with a staggered array of cylindrical obstacles giving an average blockage ratio of 40% is used to examine quasi-detonation propagation.

Shown in Fig. 3 is the trajectory of a flame in a stoichiometric methane–air mixture propagating down this tube. The flame accelerates within 3–4 m (10–12 tube diameters) to a velocity of 1000 m/s. This velocity is more than 200 m/s greater than the maximum turbulent flame velocity that was previously observed in a stoichiometric methane–air mixture in a similar diameter tube with orifice-plate obstacles [4]. Thus, the obstacle geometry can play a significant role in the acceleration and terminal velocity of a turbulent flame. The methane–air flame does not transit to detonation ($V_{CJ}$ = 1.8 km/s), however. Indeed, a methane–air mixture has never been shown to detonate under laboratory conditions, because it is an extremely insensitive mixture with a detonation cell size on the order of 30 cm. In order for a detonation to propagate, the tube diameter must typically be at least one cell width in diameter. In Fig. 3, the fact that the passage between obstacles is less than one cell width effectively "denies" the turbulent flame the ability to detonate. To make the final transition to detonation, the length scales of the tube must be consistent with the chemical length scales of the explosive mixture (induction length, cell size, etc.). This limit is not so easily overcome, and requires that the mixture be conditioned or sensitized in some way to reduce the relevant chemical length scale.





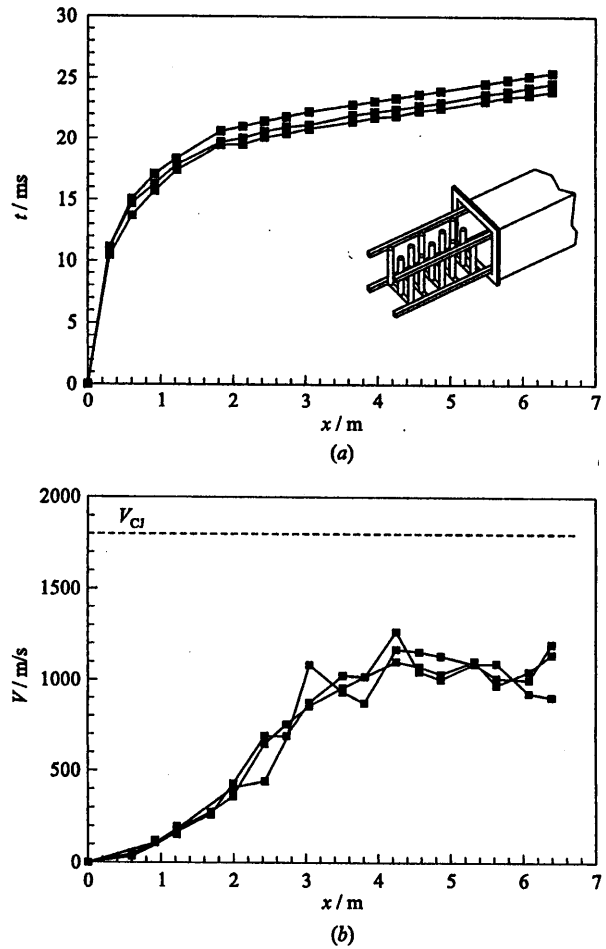


**Figure 3** Time vs. distance (*a*) and velocity vs. distance (*b*) data for turbulent flame acceleration in a square channel (30×30 cm) with regularly spaced, cylindrical obstacles and stoichiometric methane–air mixture (initial pressure 1 bar)

# 4 ONSET OF DETONATION: SENSITIVITY OF MIXTURE

While chemical kinetics plays a role in laminar and turbulent flame propagation, it is only with the shock-initiated reactions of the final onset of detonation that the exponential nature of kinetic rates dominates the propagation mechanism. Compared to laminar–turbulent flame transition and the acceleration of turbulent flames, chemical sensitization or desensitization of combustible gases for detonability has received comparatively little attention. The work that is available suggests that halogenated compounds, typically thought of as inhibitors for flammability, may in fact act as sensitizers for detonation. Moen *et al.* [24] and Vandermeiren and Van Tiggelen [25] both found that $CF_3Br$ had a slight sensitizing effect on hydrocarbon–air detonations. Likewise, Egerton and Gates [26, 27] found that lead tetraethyl (an antiknock agent) resulted in a reduced length for transition to detonation, despite the compound's expected role as a scavenger of free radicals. Later experiments by Shchelkin and Sokolik [28] with increased concentrations of lead tetraethyl did show an increase in the length required for transition to detonation.

Given the limited data available on sensitization of detonable mixtures, the most significant effect was demonstrated by the cool flame experiment of Shchelkin and Sokolik [29]. They injected a mixture of pentane and oxygen (250–370 Torr) into a heated tube (325–400 °C) and ignited the mixture at one end after a specified delay. If the delay was longer than the half-second period required for a cool flame oxidation process to be effected, a significant reduction in the length required for the mixture to detonate was observed (from 80 to 40 cm). Their conclusion was that the presence of relatively long-lived peroxide radicals in mixtures processed by cool flame oxidation resulted in significantly increased kinetic rates and thus a reduction in the run-up distance to detonation.

In order to further investigate the role of free radicals on the length scales required for DDT, Yoshinaka *et al.* [30, 31] have recently conducted an investigation using a system of gaseous hydrogen and chlorine. This system permits the use of a UV light source to photochemically dissociate the molecular chlorine into chlorine radicals, thus uniformly presensitizing a quiescent mixture. The schematic of the experiment is shown in Fig. 4. For a mixture of $1.5H_2 + Cl_2$ at 4.8 kPa, steady illumination from the UV light will result in the mixture undergoing autoignition after approximately 200 ms. If the mixture is ignited at one end via a weak spark prior to autoignition, the effect of free radicals on the transition to detonation can be observed. Figure 5 shows the velocity of the combustion wave (as monitored by photodiodes mounted along the tube) for experiments with and without UV presensitization. Note that the envelopes shown enclose ten repeated experiments for both cases (with





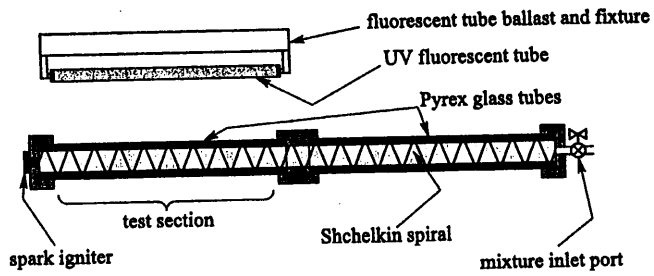


**Figure 4** Schematic of experiment to examine the effect on DDT of free radicals created in hydrogen–chlorine mixtures by UV light

and without UV irradiation) to incorporate the inherent scatter present in any DDT experiment. The flame trajectories agree for the two cases until the flame reaches approximately 1000 m/s, whereupon the UV-sensitized mixture promptly transitions to detonation with a significant overshoot of the CJ velocity, while the unsensitized mixture takes approximately 20% longer to initiate and does so only after a period of nearly constant velocity flame propagation. This result reinforces the idea that the effect of chain-initiating chemical radicals, and therefore the role of kinetic rates in general, only becomes significant in the final stages of DDT when shock-initiated reactions are the propagation mechanism.

Other than the cool flame experiment of Shchelkin and Sokolik [29], a similar presensitization of hydrocarbon–air mixtures has not been demonstrated. For PDE applications, additives such as acetylene [32], nitrates such as isopropyl nitrate [33, 34], and conventional fuel additives dimethyl ether (DME) and 2-ethylhexyl nitrate (2-EHN) [35] are currently being considered as sensitizers to reduce the length scales of hydrocarbon–air detonations.

Based on detonation cell size, acetylene is the most sensitive of any hydrocarbon fuel in air and thus is an obvious candidate as a sensitizing agent for fuel–air mixtures. Such a sensitization effect is observed in natural gas [36]. The addition of relatively small amounts (5%) of ethane to methane, such as found in natural gas, results in the induction time being reduced by a factor of two, thus rendering the mixture much more sensitive than pure methane. Recent results obtained at McGill University, however, suggest that acetylene's role as a sensitizer of hydrocarbon fuels is merely a linear interpolation between the unsensitized mixture and pure acetylene in air. Figure 6 shows results for a propane–acetylene–oxygen–nitrogen mixture where the oxygen-to-nitrogen ratio is fixed at $\beta = 3.0$ (corresponding to oxygen-enriched air). As the percentage of acetylene in the fuel ($\alpha$) is changed, the oxygen concentration is varied

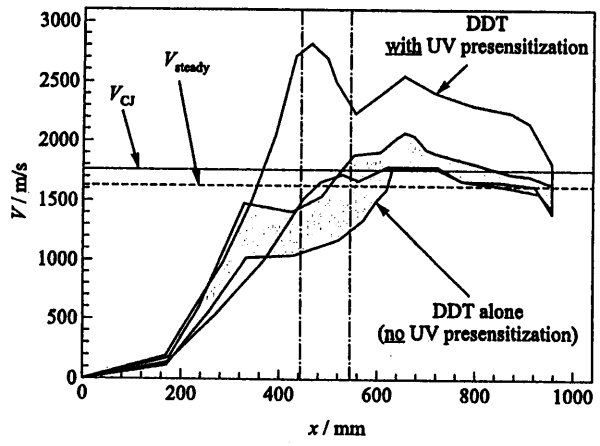


**Figure 5** Velocity vs. distance data demonstrating the effect of UV presensitization for $1.5H_2 + Cl_2$ mixtures at initial pressure 4.8 kPa

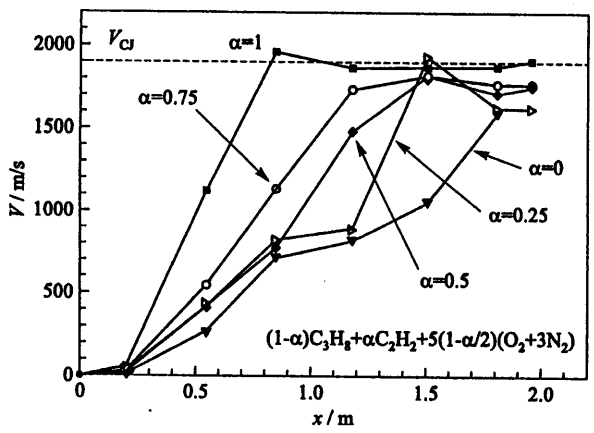


**Figure 6** Velocity vs. distance data showing the effect on DDT of adding acetylene to a propane–oxygen–nitrogen mixture (constant stoichiometry, initial pressure 1 bar)





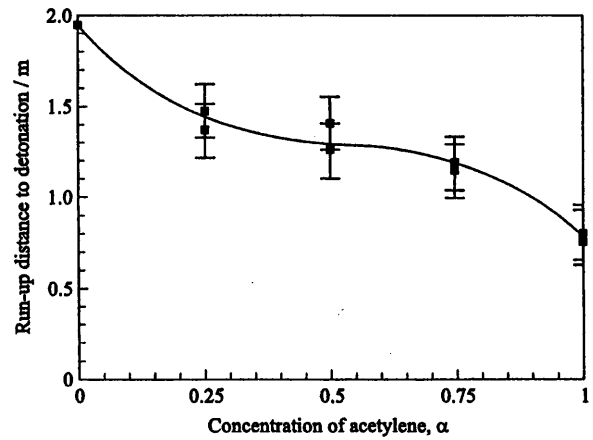


**Figure 7** Reduction in run-up distance to detonation as a function of acetylene concentration

to maintain a stoichiometric fuel equivalence ratio. The velocity of the combustion wave as measured by ionization probes along the tube is plotted in Fig. 6 (the details of the apparatus are the same as for Fig. 2). The run-up distance to detonation as a function of $\alpha$ is plotted in Fig. 7, and the addition of a small amount of acetylene is not seen to have the desired sensitization effect.

The addition of various nitrates (isopropyl nitrate, 2-ethylhexyl nitrate, etc.) to a hydrocarbon fuel is suggested to have an effect due to the formation of $NO_2$ by the decomposition of the nitrate, which reacts with methyl radicals to produce OH radicals [33]. Rather than investigate the effect of these various nitrates, which is complicated by their typically low vapor pressure at room temperature, a preliminary investigation of direct $NO_2$ addition to hydrocarbon–air mixtures has recently been done at McGill University. Again using propane in oxygen-enriched air as a baseline mixture, $NO_2$ was added to the mixture and the effect of different concentrations was observed. The baseline mixture was slightly propane-rich in oxygen-enriched air: mixture (a) $C_3H_8 + 5(0.95O_2 + 3N_2)$ at initial pressure of 1 bar. The result of 10 repeated experiments in mixture (a) is shown as a shaded envelope in Fig. 8. Adding 0.5 Torr of $NO_2$ to mixture (a), representing $\sim$ 1% addition to the fuel content, resulted in no noticeable change in the run-up distance to detonation. Increasing the $NO_2$ concentration to 4 Torr or $\sim$ 10% addition to the fuel, resulted in a shortening of the run-up distance to detonation by 0.3 m (corresponding to

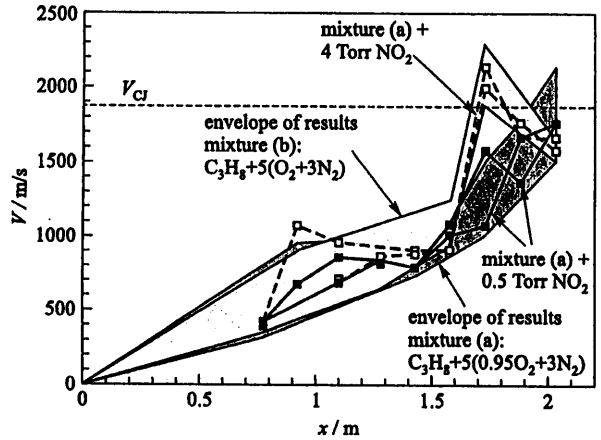


**Figure 8** Velocity vs. distance data showing the effect on DDT of adding $NO_2$ to a propane–oxygen–nitrogen mixture (initial pressure 1 bar)

two tube diameters), but this same reduction in run-up length can also be effected by increasing the oxygen partial pressure by 9 Torr, bringing the mixture to stoichiometric, (mixture (b)). Since the effect of $NO_2$ addition is comparable to simply adding oxygen, it may merely result in an energetic effect rather than a chemical sensitization that significantly accelerates the kinetic rates*. These results suggest that $NO_2$ is not an effective sensitizer. Nitrates that decompose to form $NO_2$ do not appear to have a very significant sensitization effect either [33, 34]. An additive that plays a substantial role in accelerating the chain initiation and branching mechanisms has yet to be identified.

## 5 CONCLUDING REMARKS

As DDT is an extremely complex phenomenon, incorporating numerous different mechanisms and orders of magnitude variations in propagation velocity, it is essential that studies of DDT carefully isolate the effect being examined. The results reviewed in this paper showed that the effect of a spark igniter for fuel–air

*Note that $NO_2$ is partially polymerized to the dimer $N_2O_4$ at room temperature (30% $NO_2$, 70% $N_2O_4$ at 20 °C). Thus, the effect of adding $NO_2/N_2O_4$ should be compared to adding an equivalent number of oxygen atoms.





mixtures is confined to promoting a more rapid transition from laminar to turbulent flame and does not significantly influence the run-up distance required for detonation. Only with a turbulent jet igniter of very large diameter ($d > 10\lambda$) can the intensities and scales of turbulence necessary for the direct onset of detonation be realized. Obstacles on the tube wall can increase the intensity of turbulence in the flame and introduce transverse pressure fluctuations (shocks), and thus dramatically increase the burning rate and strength of compression waves sent ahead of the flame. This sets the stage for shock-induced combustion and the onset of detonation by the formation of explosion centers, but detonation will not occur if the tube is smaller than the characteristic detonation length scale (the cell size). It is in this final onset of detonation that kinetic rates dominate the transition mechanism and the presence of free radicals or other chemical sensitizers can have a pronounced effect. An efficacious sensitizer for hydrocarbon fuel–air mixtures has yet to be identified, but the cool-flame experiments of Shchelkin and Sokolik [29], in which a heavy hydrocarbon fuel is re-formed via a partial oxidation process to more sensitive hydrocarbons and free radicals, appears to be a promising way to dramatically reduce the transition length to detonation.

In light of the fact that DDT is an ensemble of various mechanisms, the results reported in this paper represent the same shortcomings as prior work in DDT: examining the run-up distance to detonation alone does not isolate the various mechanisms involved. Rather, future work on DDT should be focused on defining the basic scaling laws for DDT, and then relating these laws to more fundamental parameters, such as the ratio of mixture cell size to tube diameter.

## ACKNOWLEDGMENTS

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## Appendix 2: Jet Initiation of Detonation via Rapid Constant Volume Explosion

Higgins, A.J., "Jet Initiation of Detonation via Rapid Constant Volume Explosion," unpublished results, McGill University, 2002.

# Jet Initiation of Detonation via Rapid Constant Volume Explosion

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## 1. Introduction

The ability to initiate detonation in a hydrocarbon fuel/air mixture without the use of an oxygen-based predetonator would be a highly advantageous option for Pulse Detonation Engines. Elimination of the requirement to carry (or generate) on-board oxygen would offer considerable performance and logistical advantages. Due to the large energy requirements ($\approx$ 100-1000 kJ), direct initiation of hydrocarbon fuel/air detonations is not an option. Thus, the energy contained in the combustible fuel/air mixture itself must be used.

The fact that a turbulent jet of combustion products can directly initiate a detonation is well established in the literature.[1-9] Most of these studies, however, used flame jets emerging from long tubes or previously established detonations to drive a turbulent jet of combustion products. These are clearly not an option for a Pulse Detonation Engine. This study focused on using a small volume prechamber of combustible gas (same gas as in main detonation chamber) to drive the turbulent jet. Various techniques of creating a nearly constant volume explosion in the precombustion chamber were explored. In order to drive as intense a jet as possible, it is necessary to effectively burn all of the gas in the precombustion chamber "instantaneously." The timescale required for effectively instantaneous burn-out is determined by the acoustic timescale of the precombustion chamber. Since sound in air propagates at 350 m/s (35 cm/msec), it is necessary to burn-out the volume of gas on millisecond timescales. If burn-out takes longer, the gas in the precombustion chamber will begin to vent through the orifice plate into the main detonation tube before peak pressures are reached.

Once viable techniques to create constant-volume explosion were realized, the techniques were used to drive turbulent jets of combustion products through various orifice plate designs. The ability to initiate a detonation in the main detonation tube was quantified by varying the nitrogen dilution of the propane/oxygen mixture used. The critical mixture for detonation to be obtained was identified, and this value was used to compare the various orifice plates and precombustion chamber burn-out techniques. The scaling of these results to a larger apparatus was also studied.

## 2. Apparatus

### 2.1 6.35 cm Tube

The main experimental apparatus used in these experiments is a 6.35 cm internal diameter stainless steel detonation tube. This tube is comprised of segments 30 cm long, which can be joined together or used individually (Fig. 1). For the Constant Volume Explosion experiments (Section. 3.1), only a single tube is used for the constant volume

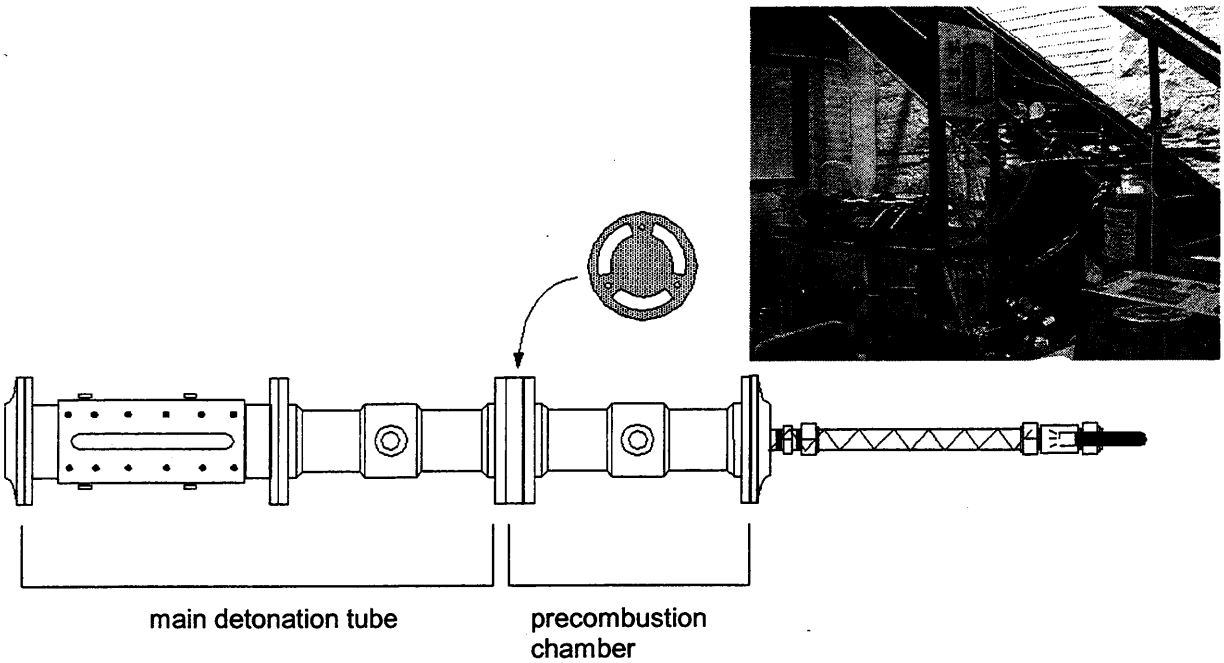



**Fig. 1.** 6.35-cm-diameter apparatus for constant volume explosion chamber and jet initiation of detonation.

explosion chamber (although additional tubes are used to house the multiple flame jet tubes).

The mixtures for this apparatus are prepared by co-flowing the three gases (propane/nitrogen/oxygen) simultaneously through three separate choked orifices, and then mixing the gases in-line before entering the tube. The flow rates are set using a micrometering orifice, and measured using rotometers. The rotometers were previously calibrated using the soap-bubble technique. The chamber was evacuated prior to filling. The mixtures used were stoichiometric propane/oxygen, with variable nitrogen dilution, at an initial pressure of 1 atm.

For the constant volume explosion experiments, a pressure transducer (PCB 113) is used to record the peak pressure and the time required to reach the peak pressure. For the detonation initiation experiments, two transducers, spaced four tube diameters apart beginning approximately two tube diameters downstream of the orifice plate, were used to determine if initiation was successful. The successful initiation of a detonation was clearly identified by the characteristic pressure trace and an average wave velocity between the two transducers approximately equal to the CJ velocity. Failure to initiate was denoted by a weak shock wave followed by combustion activity on the pressure transducer trace, and average wave velocities typically at half of the CJ velocity.

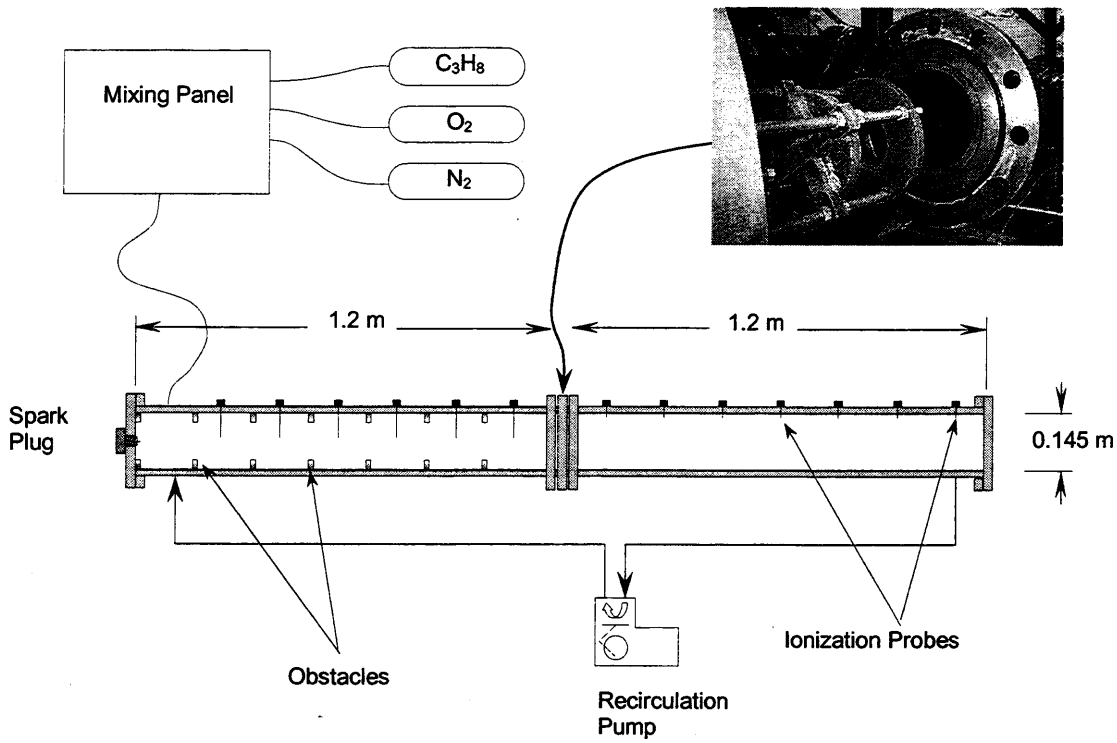



**Fig. 2.** 14.5-cm-diameter detonation tube.

An approximately 30 mJ spark was used for ignition. In the case where multiple sparks were used, the same ignition circuit was connected to each spark gap in series, so that all sparks were ensured to fire simultaneously.

## 2.2 14.5 cm Tube

In order to determine how the results obtained in the 6.35 cm diameter tube scaled, tests were also performed in a 14.5-cm-internal-diameter detonation tube. In this apparatus, the first 1.2-m length of tube served as the precombustion chamber (Fig. 2). While this is not representative of the size of the precombustion chamber that could be used in a PDE, only a single-spark ignition was used. The combustion wave in the precombustion chamber was monitored, and its velocity did not exceed 1 km/s in these tests. Thus, the conditions driving the combustion jet should be representative of a constant volume explosion that could be created by the techniques developed with the 6.35 cm apparatus.

The propane/oxygen/nitrogen mixtures in this apparatus were prepared by first evacuating the tube, then partial pressure filling each gas in sequence, followed by recirculation for at least 30 minutes using a bellows-type pump. Results were monitored with ionization probes mounted along the length of the test section. The same ignition circuit was used for this apparatus.

# 3. Results

## 3.1 Constant Volume Explosion

The results with a single spark in the precombustion chamber (sealed with a closed flange at each end) are shown in Fig. 3a, showing the pressure recorded by a pressure transducer mounted in the chamber. Note that approximately 100 msec is required to reach the peak pressure for this fuel/air mixture ($\beta = 3.76$). In Fig. 3b, a single flame tube is added to the precombustion chamber, so that the spark ignites a flame which in turn jets into the chamber. The time required to reach peak pressure is observed to decrease by a factor of approximately ten, compared to the result shown in Fig. 3a (note different timescales on $x$-axis). Figure 4 shows the pressure ratio reached and the time to reach peak pressure as a function of the nitrogen dilution $\beta$ for a single spark. The ideal constant volume explosion pressure as predicted by chemical equilibrium is also plotted. Note that there is a consistent offset between the predicted and observed peak pressures owing to heat losses to the chamber walls. As the nitrogen dilution increases, the time required to reach the peak pressure increases significantly, reaching a value greater than 100 msec as the value of $\beta$ approached 3.76 (corresponding to air). This result clearly demonstrates that a single spark is not sufficient to create an effectively instantaneous constant volume explosion in a propane/air mixture.

Figure 5 shows additional results with a single flame tube and an array of 6 flame tubes (see Fig. 6 for schematics of techniques used). The addition of a single flame tube has a significant effect on reducing the time to reach peak pressure. The time-to-peak is on the order of a few msec's up to a $\beta$ value of 3 (where a single spark requires 100 msec to reach peak pressure). By increasing the number of flame tubes, the time to peak can be kept at millisecond timescales all the way to fuel-air mixtures ($\beta = 3.76$). Note, however, that the addition of such a large number of flame tubes results in lowering the peak

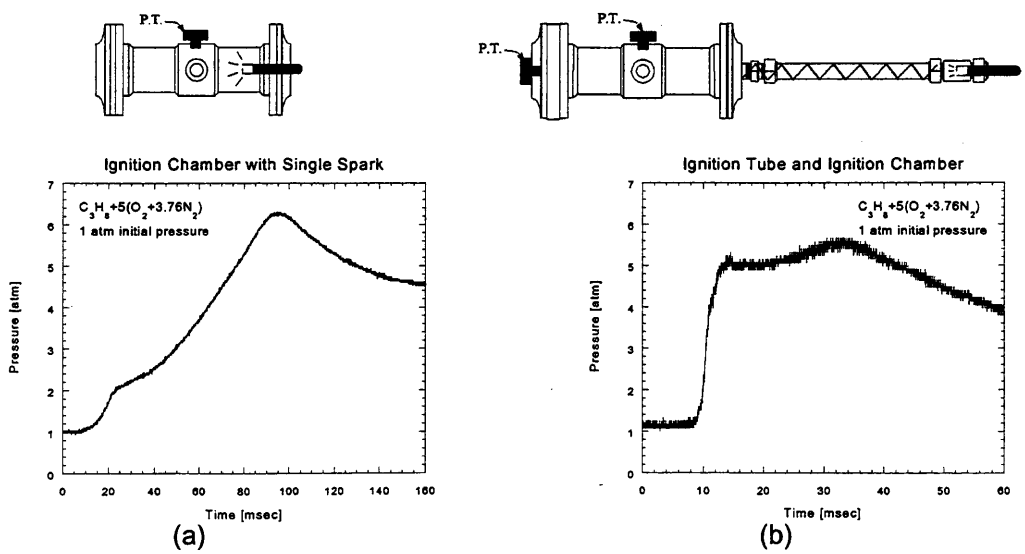



**Fig. 3.** Pressure trace from precombustion chamber (closed) with (a) single spark ignition and (b) a single flame tube.

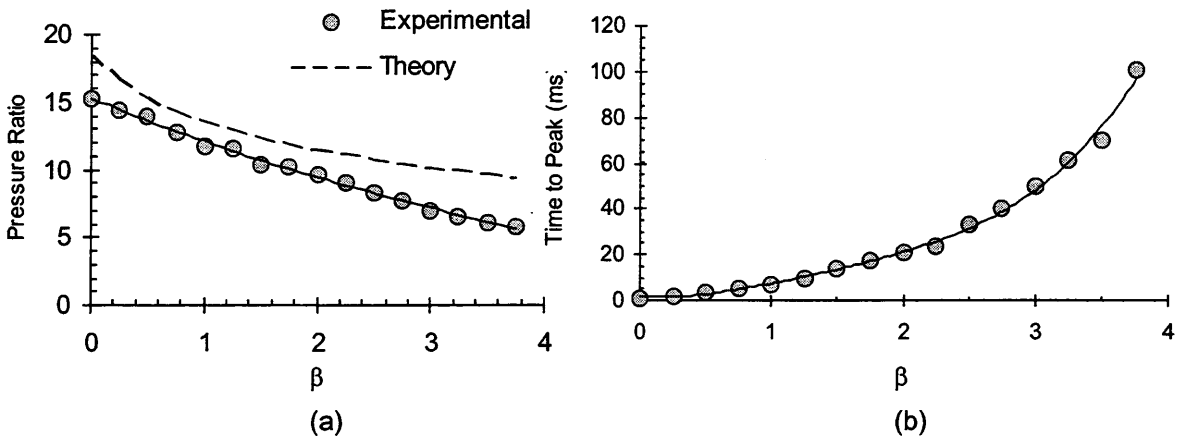



**Fig. 4.** (a) Pressure ratio and (b) time to peak pressure as a function of nitrogen dilution for single-spark ignition.

pressures reached in the chamber. At $\beta = 3.76$, the pressure obtained with 6 flame tubes was approximately 2 atm, compared to 5 atm for a single spark or single flame tube. This lowering in the peak pressure obtained was attributed to heat losses to the internal area of the flame tubes.

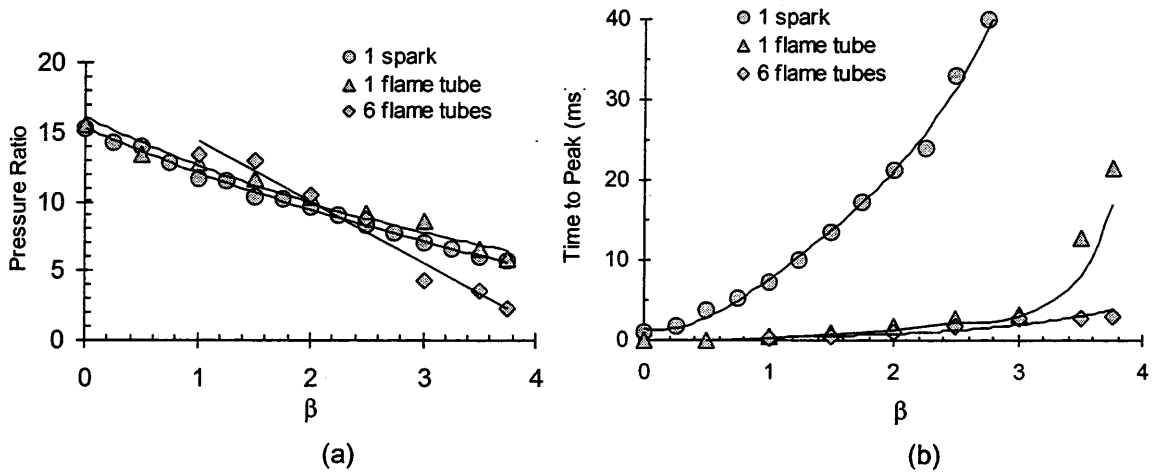



**Fig. 5.** (a) Pressure ratio and (b) time to peak pressure as a function of nitrogen dilution for single spark, single flame tube, and multiple flame tubes.

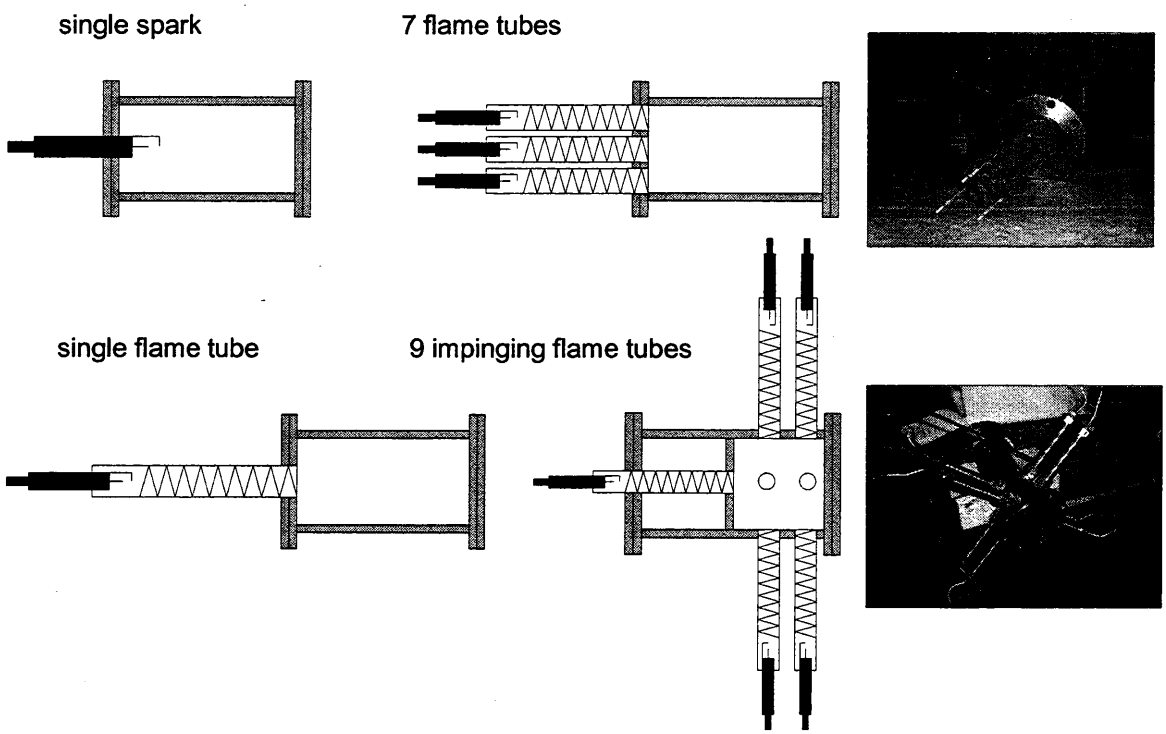



**Fig. 6.** Schematic of techniques used to create constant volume explosion in precombustion chamber.

## 3.2 Jet Initiation in 6.35 cm Tube

The precombustion chambers investigated in Section 3.1 were used to drive jets of combustion products into the main detonation tube, which was of identical diameter as the precombustion chamber. The orifice plates used between the precombustion chamber and the main detonation tube are shown in Fig. 7. Both chambers contained identical mixtures for all tests. The nitrogen dilution $\beta$ was varied in order to identify the critical value that permitted initiation of detonation to occur in the main detonation tube within 6 tube diameters of the orifice plate. Examining the result of an experiment at this location is somewhat arbitrary and is dictated by the location of instrument ports. However, since all mixtures, even propane/air, will eventually detonate on their own via the DDT mechanism if given a long enough tube, it is necessary to establish a threshold length scale. To some extent, this definition will always be arbitrary.

The results are summarized in Table 1, where the critical values of $\beta$ are reported. In this table, rows correspond to the technique used to burn-out the precombustion chamber and columns correspond to different orifice plate designs. A range of values is reported in many cases: the lower value of $\beta$ corresponds to cases when detonation was always initiated and the upper value is when detonation was not initiated, out of several repeated trials. The higher the value of $\beta$, the more successful the initiation technique (i.e., the mixture can more closely approach propane/air in mixture sensitivity and still be initiated).

Note that a single spark plug in an open tube (no orifice plate) is the least effective initiator; it cannot initiate detonation above $\beta = 0.5$. The annular orifice plates appear to be the most effective, permitting mixtures with $\beta$ values of up to 2.125 to be initiated. Interestingly, the results with the annular orifice plate do not appear to be very sensitive to the technique used to burn out the precombustion chamber. In fact, the use of a single spark plug or single flame tube to burn-out the precombustion chamber appears to be almost as effective as using multiple flame tubes. Increasing the number of flame tubes to 9 actually decreases the effectiveness of the initiation technique, lowering the maximum mixture sensitivity to $\beta = 1.35$. This may be due to the previously noted fact that, as more flame tubes are added, the peak pressure reached decreases due to heat losses to the flame tube surface area.

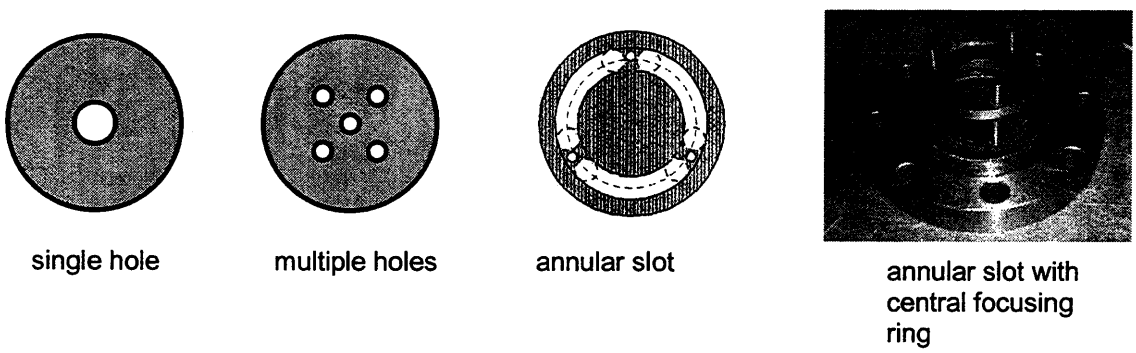


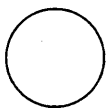
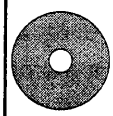
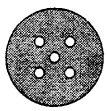
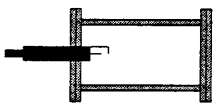
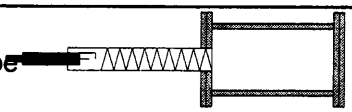
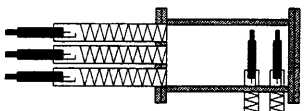
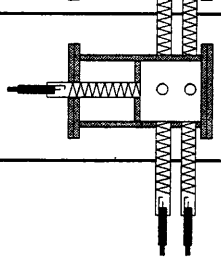

**Fig. 7.** Orifice plates used for jet initiation of detonation.

**Table 1**: Results with different techniques of jet initiation in terms of mixture dilution.

| β values reported for critical case of detonation within 2-6 tube diameters of orifice plate. | Open Tube | Hole (0.5") | Multiple Holes (5 x 0.225") | Annular Slot (3/8" width) | Annular Slot with Ring (side view) |
|---|---|---|---|---|---|
| Single Spark | 0.5 | | | | 1.5 – 1.75 |
| Single Flame Tube | 1.125 – 1.25 | 0.875 – 1.00 | 1.125 | 1.5 – 1.75 | 1.5 – 2.125 |
| Multiple (6) Flame Tubes | 1.375 | 0.75 – 1.00 | 1.25 | 1.625 – 2.00 | 1.75 – 2.125 |
| Impinging Flame Tubes (9) | 1.00 | 0.75 – 1.125 | 0.75 – 1.375 | 1.375 | 1.25 – 1.375 |

In Table 2, the same results are reported, now using the characteristic detonation cell size to normalize the diameter of the jet (equal to diameter of tube). Here, the *smaller* the value of $D/\lambda$, the *more* effective the initiation technique (meaning: less sensitive mixtures can be initiated). The best scenario identified (i.e., using flame tube(s) to drive a jet of combustion products through a centrally focused annular jet) can initiate detonation for a $D/\lambda$ value of 4.

**Table 2**: Results with different techniques of jet initiation in terms of $D/\lambda$.

| Tube diameter $D$ normalized by cell size $\lambda$ for critical case of detonation within 2-6 tube diameters of orifice plate. | Open Tube  | Hole (0.5")  | Multiple Holes (5 x 0.225")  | Annular Slot (3/8" width)  | Annular Slot with Ring (side view)  |
|---|---|---|---|---|---|
| Single Spark  | 30 | | | | 5 |
| Single Flame Tube  | 10 | 16 | 12 | 5 | 4 |
| Multiple (6) Flame Tubes  | 8 | 16 | 10 | 4 | 4 |
| Impinging Flame Tubes (9)  | 16 | 12 | 8 | 8 | 8 |

## 3.3 Jet Initiation in 14.5 cm Tube

In order to see if the results in the prior section scale to larger apparatus and less sensitive mixtures, experiments were performed in a 14.5-cm-diameter tube. A 1.2-m-long obstacle-laden detonation tube was used as the precombustion chamber. Although this tube is longer than the precombustion chamber used previously, it is only initiated by a single spark, and the velocities obtained do not exceed 1 km/s. Thus, it is believed that the conditions in this tube are representative of constant volume explosion conditions.

First, control experiments were done with no orifice plate and the combustion wave leaves the precombustion chamber and enters a smooth-walled tube. The results are shown in Fig. 8. Beyond a nitrogen dilution of $\beta = 2.25$, the mixture is unable to transition to detonation when it leaves the precombustion chamber with obstacles. When an annular orifice plate with central-focusing ring is added (Fig. 9), the mixture in the

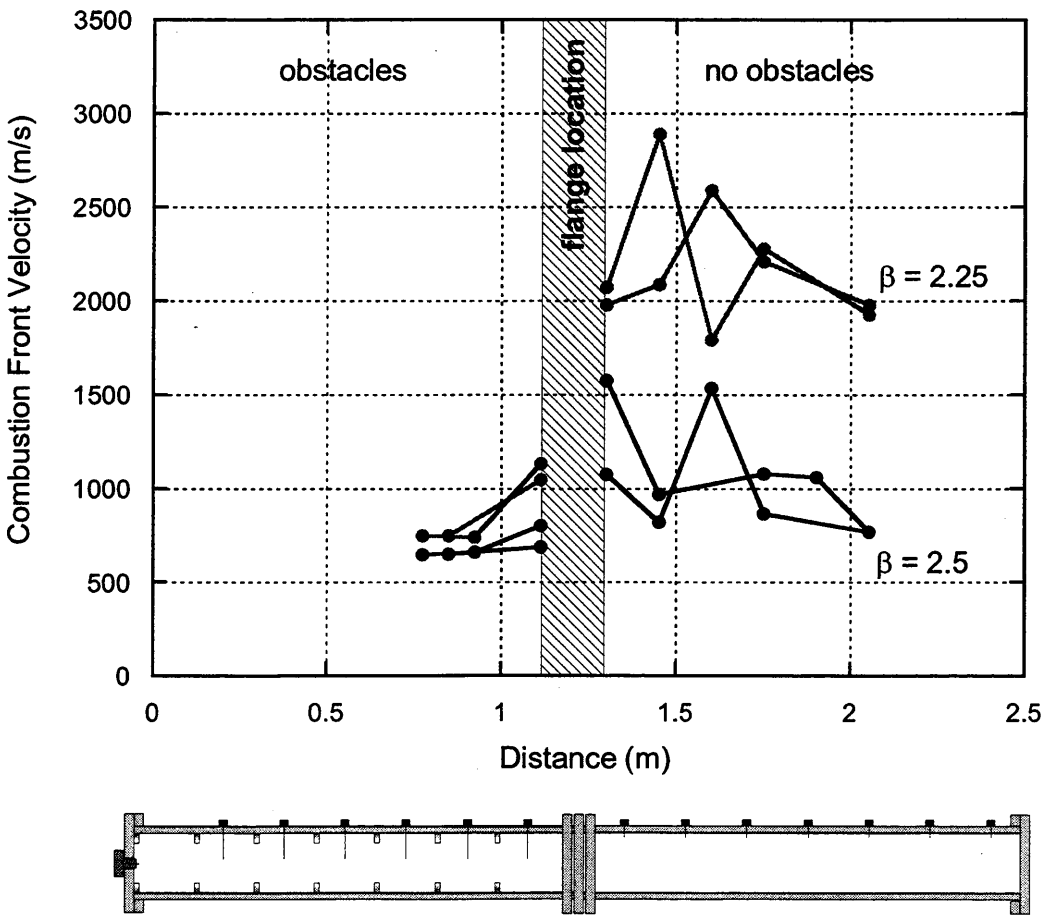



**Fig. 8.** Results with no orifice plate between obstacle-laden precombustion tube and smooth-walled tube.

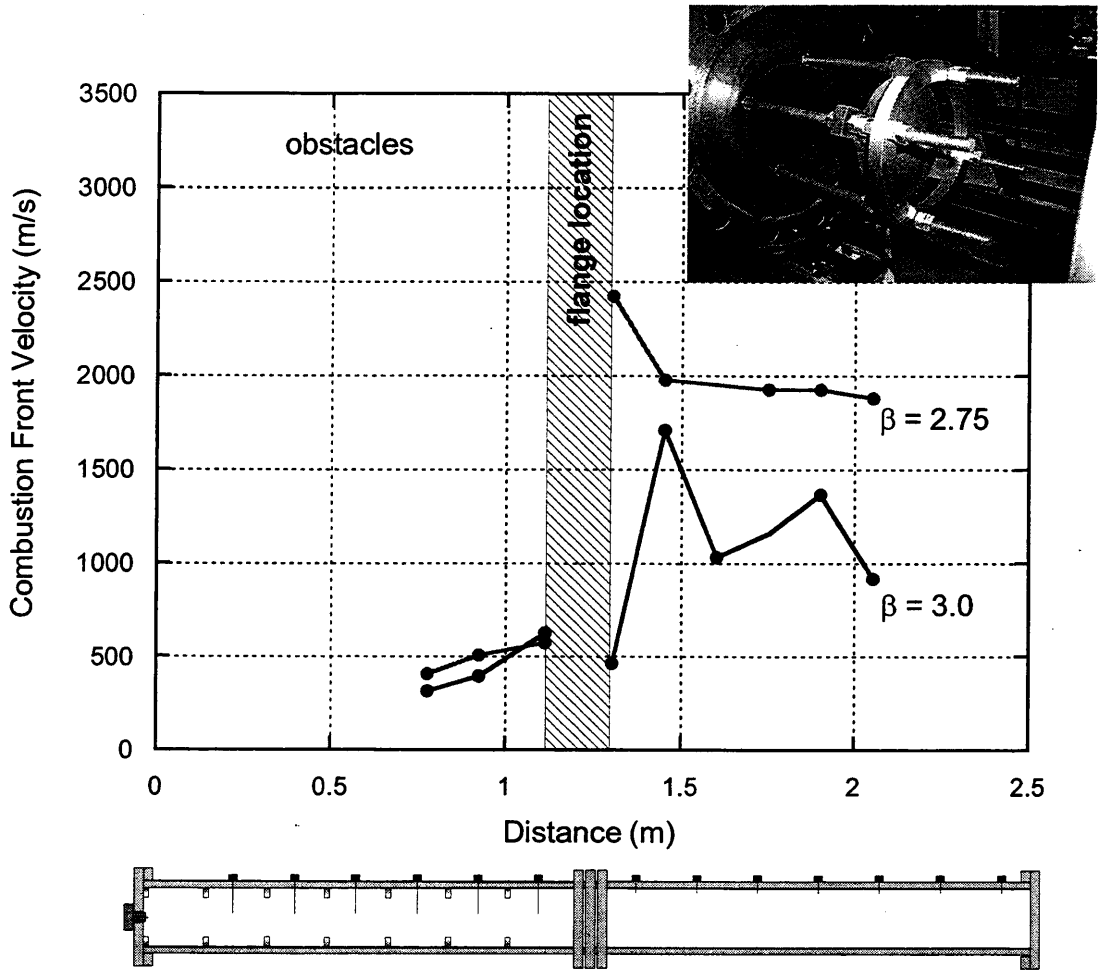



**Fig. 9.** Results using annular orifice plate with focusing ring between obstacle-laden precombustion tube and smooth-walled tube.

smooth-walled tube is able to be detonated up to a mixture of $\beta = 2.75$. While this increase in the critical value of $\beta$ may seem small (from 2.25 to 2.75), it is worth recalling that the characteristic cell size (an inverse measure of mixture sensitivity) increases from approximately 18 mm to 30 mm over this range (see Fig. 10).

The diameter of the jet (14.5 cm) normalized by the cell size $\lambda$ lies in the range of $D/\lambda = 4\text{-}5$ for this configuration. This result confirms that the results obtained in the small 6.35-cm-diameter apparatus can be successfully scaled by cell size to apply to large scales and less sensitive mixtures.

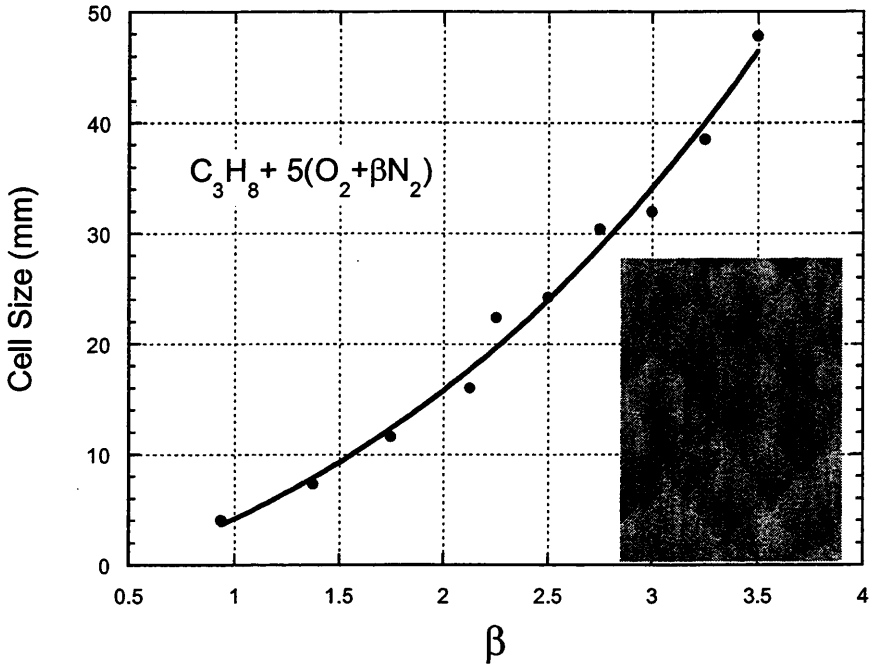



**Fig. 10.** Detonation cell size λ as a function of nitrogen dilution.

## 4. Conclusions

The results of this study show that initiation of detonation via a jet driven by a precombustion chamber is feasible. A variety of techniques to burn-out the precombustion chamber were investigated. The use of a single or multiple flame tubes was identified as being the most effective. The use of more flame tubes resulted in a more rapid burn-out, but the peak pressures reached were lower. This lower peak pressure may be responsible for the less effective initiation observed when multiple impinging flame tubes were used to drive the jet.

The results with the 6.35-cm-diameter apparatus and the 14.5-cm-diameter apparatus could both be scaled with the detonation cell size. The diameter of the optimized jet in both cases was 4-5 times the characteristic cell size of the mixture being initiated. This result suggests that stoichiometric propane/air mixtures at 1 atm could be initiated by a similar technique if the apparatus diameter were scaled up to 20 cm (8 inch) in diameter.

The size of the precombustion chamber was not systematically studied; however, simple considerations suggest that it should be at least one tube diameter long. If the precombustion chamber is several tube diameters long, it is unlikely that the entire volume of burned gas can contribute to the jet on the initiation timescales. Thus, the volume of chamber used here (length approximately four tube diameters) is probably near optimal.

These results suggest a general strategy to attack the problem of initiating fuel/air detonations in a PDE without the use of an oxygen-based predetonator: by using a "cascade" of ever quickening ignition mechanisms (weak spark → flame tube →

precombustion chamber → jet), a very rapid rate of chemical energy release can be created in the main detonation chamber. However, the rate of pressure increase is not the only factor to consider; as identified here, the peak pressure is also important, and addition of superfluous flame tubes can have a deleterious effect by increasing surface area and heat losses.

## 5. Acknowledgements

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## Appendix 3: The Effects of $NO_2$ Addition on Deflagration-to-Detonation Transition

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# The effects of $NO_2$ addition on deflagration-to-detonation transition

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**Abstract**

The chemical sensitization of hydrocarbon–air mixtures to detonation initiation has been studied. Experiments were carried out in order to evaluate the effect of $NO_2$ addition to propane ($C_3H_8$)–oxygen ($O_2$)–nitrogen ($N_2$) mixtures at ambient conditions. The run-up distance and detonation cell size were established for $C_3H_8$–$O_2$–$N_2$ mixtures without $NO_2$ and with $NO_2$ added as a 10 to 50% fuel additive. The results show that the addition of $NO_2$ causes no change in either the run-up distance or the cell width, indicating that the kinetic changes brought about by the $NO_2$ are not significant to the initiation of detonation. This result is shown to agree with kinetic models that suggest that $NO_2$ is not very effective at promoting ignition at very high temperatures such as that characteristic of detonations.


*Keywords:* Nitric oxides; Detonations; Transition to detonation; Fuel sensitizers

## 1. Introduction

Renewed interest in detonations for propulsion applications has focused attention on the problem of deflagration-to-detonation transition (DDT) in fuel–air mixtures. A prohibitively large deposition of energy is required for direct initiation of higher hydrocarbon fuels in air. Consequently, methods are being sought to reduce the run-up distance required for DDT. In light of previous results relating the effects of fuel additives on ignition delay and detonation properties such as cell size, it has been proposed that nitrates could potentially offer a means to radically enhance the sensitivity of hydrocarbon fuels to detonation. Nitrates are commonly used as additives in diesel fuels. Indeed, many studies have shown that compounds such as isopropyl nitrate (IPN) and ethylhexyl nitrate (EHN) tend to promote diesel ignition by reducing the ignition delay of the fuel–air mixture [1,2]. The local temperature and equivalence ratio typical of these applications at the location of ignition ($\sim$ 850 K and $\varphi \sim 3$–4 [3]) is far from those typical of detonation initiation ($\sim$ 1600 K and $\varphi \sim 1$); nevertheless, with the growing interest in detonation and supersonic combustion for propulsion applications, it has been proposed that nitrates may result in analogous sensitizing effects for hydrocarbon fuel detonations.

Studies of the effect of this type of additive on simple ignition delay of hydrocarbon fuels reveal mixed results. Davidson et al. [4] and Sidhu et al. [5] have studied the effect of EHN addition on hydrocarbon fuel ignition. Davidson reported little change in the induction time for 180 ppm of 2-EHN in *n*-heptane–$O_2$–Ar, while Sidhu used 1% EHN in JP-7 and JP-8 and reported 5 to 20% reduction in induction time. An extensive study of a variety of additives including peroxides, esters, polyethers, and alcohols at 950 to 1300 K by Siminski and Wright [6] indicated that nitrate and nitrite esters were most effective in promot-

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ing hydrocarbon ignition. These thermally decompose into nitrogen oxides and alkoxy radicals, both of which can lead to accelerated ignition. Further, experiments with compounds yielding almost exclusively alkoxy radicals vs experiments with pure NO and $NO_2$ indicated that the nitrogen oxides were most effective in promoting ignition.

Experimental investigations of the effect of this type of additive on detonations have also been reported. Zhang et al. [7] studied the effect of IPN on the detonation sensitivity of hexane. They demonstrated that the detonation cell width of hexane–IPN–air mixtures decreased as the IPN concentration increased. However, to achieve a 50% reduction in cell width, approximately equal amounts of IPN and fuel were required. This substantial amount of IPN resulted in an increase in the Chapman–Jouguet (CJ) velocity, indicating a change in the energetics of the mixture. IPN cannot be considered a sensitizer in this case, since sensitization should require only a small amount of additive, without affecting the energetics of the mixture. In a more recent study, Hitch [8] used 10 vol% IPN in propane and reported no change in the distance for transition from deflagration to detonation. An extensive study by Tieszen et al. [9] compared cell width measurements and computed ZND induction length of a number of fuel–air mixtures. The measurements demonstrated that the cell width of some compounds comprising an alkyl radical and a nitro or nitrate functional group is much smaller than the cell width of the parent alkane. Using the example of nitroethane in air, they explain that the low bond energy between the functional group and the alkyl radical is easily broken, leaving an ethyl radical and $NO_2$. The ethyl radical then decomposes into ethylene and H atoms, which can react with $NO_2$ to produce OH.

In this study, we sought to evaluate the sensitizing effect of $NO_2$ proper on hydrocarbon fuel detonations. The effect was evaluated by comparing both the run-up distance to detonation and the cell size for propane–oxygen–nitrogen mixtures both with and without $NO_2$ addition, but with insignificant energetic differences. The run-up distance is defined as the distance required for transition from deflagration to detonation. Although this distance is a function of the tube geometry in addition to mixture sensitivity, it has been found to be very reproducible for a given mixture. It is well established that a more sensitive mixture will have a shorter run-up distance than a less sensitive mixture as well as a smaller characteristic cell size.

$NO_2$ was chosen as the candidate sensitizer to simplify the nitrate chemistry down to a minimum and because, contrary to most nitrate compounds, $NO_2$ can be used in vapor form under the experimental conditions studied. In addition to the study of Siminski and Wright [6] mentioned earlier, work by Slutskii [10] has indicated that the effect of nitrate promoters on ignition delay is a result of the $NO_2$ generated by nitrate decomposition. He suggests that $NO_2$ reduces induction time by leading to a $CH_3$ oxidation channel. Experiments by Clothier et al. [1] using either EHN as an additive to diesel fuel or $NO_2$ in the combustion chamber confirm the hypothesis that EHN acts through its decomposition, resulting in the release of $NO_2$. In the early study by Norrish and Wallace [11], it was shown that $NO_2$ reduces the ignition temperature of $CH_4$–$O_2$. They proposed that $NO_2$ results in a path for creation of O atoms.

On the other hand, the analysis of Tieszen et al. [9] cited above indicates that the generation of a fuel radical is required in addition to the functional $NO_2$ group, which implies that $NO_2$ alone may not be effective. By isolating the $NO_2$, we therefore stand to gain a better understanding of the important mechanisms in detonation initiation.

## 2. Experimental procedure

### 2.1. Experimental apparatus

The experimental setup consisted of a 4.70-m steel detonation tube with a 0.145-m internal diameter. A schematic of the setup is presented in Fig. 1. The tube was lined with obstacles to promote rapid flame acceleration [12–14]. The obstacles used were steel orifice plates, spaced 1 tube diameter apart, giving a blockage ratio (i.e., ratio of blocked area to smooth tube area) of 0.43. Previous work by Peraldi et al. [15] has indicated that optimum flame acceleration can be achieved near this value of the blockage ratio. Ionization probes, spaced 1 tube diameter apart, were located along the length of the tube to monitor the time of arrival of the combustion wave. These time of arrival signals were used to determine the average velocity of the combustion wave between adjacent probes. The ion probes extended to the centerline of the tube so that the local effect of the obstacles did not affect the time of arrival measurements. The last portion of obstacles could be removed to yield a section of smooth tube for making cell size measurements using smoked foils. The resulting smoked foil records were scanned, and the cell width was determined by taking an average over approximately 10 cells measured by hand. The error is reported as the difference between the average cell width and the maximum and minimum values measured. The use of run-up distance in addition to cell size measurements to evaluate the sensitivity of a mixture was motivated by the current interest in pulse detonation engines (PDE). The typical design parameters of a PDE require the use of a relatively insensitive fuel/air mixture and an ignition

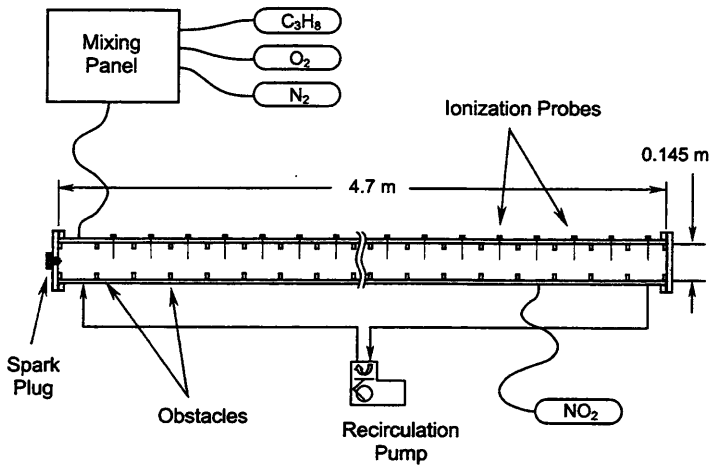


Fig. 1. Schematic of experimental apparatus.

source that is too weak to effect direct initiation of a detonation. Thus, a means of sensitizing the mixture to minimize the run-up distance is required.

### 2.2. Mixture selection and preparation

Throughout this investigation, the run-up distance and cell size were measured in mixtures of $C_3H_8$–$O_2$–$N_2$ with and without $NO_2$. Propane was chosen as the fuel for the present study since it matches the detonation sensitivity of typical jet fuels, such as JP-10 [16]. The gas mixture was prepared by evacuating the tube and then filling by the method of partial pressures to a final pressure of 1 bar. The bottled gases used were of at least 99.5% purity. Once the gases were injected, a bellows-type recirculation pump was used to thoroughly mix the gases. The mixtures were recirculated for a minimum of 15 min, displacing over 15 tube volumes. This provided excellent consistency in ignition and reproducibility in run-up distance. An automotive spark plug was used to ignite the mixture.

It is necessary to select an appropriate method to compare mixtures with and without $NO_2$ in order for the comparison to be meaningful. Since $NO_2$ is an oxidizer, its addition to an existing mixture would change the stoichiometry, thereby changing the sensitivity, the result being that $NO_2$ added to a stoichiometric or lean mixture could simply act as a diluent, while it could cause a rich mixture to approach stoichiometry. Thus, to evaluate the effect of $NO_2$ on the chemical kinetics of the reactions, an appropriate method is required for comparing mixtures with and without $NO_2$ such that energetic differences are eliminated.

We considered all the mixtures used, regardless of whether they contained $NO_2$, as a fuel ($C_3H_8$)–oxidizer (O)–diluent (N) system. The ratio of atomic oxygen to propane determines the stoichiometry, and the ratio of nitrogen to oxygen is the nitrogen dilution. When evaluating these ratios, 1 mol of $NO_2$ was therefore considered equivalent to 0.5 mol of $N_2$ and 1 mol of $O_2$. To eliminate energetic differences, the following two criteria were used. First, all the mixtures studied in the present investigation were of stoichiometric composition, i.e., there were always 10 oxygen atoms to 1 propane molecule, regardless of the source of oxygen ($O_2$ or $NO_2$). Second, it was proposed to compare mixtures with identical nitrogen dilution (i.e., the ratio of atomic nitrogen to atomic oxygen), again regardless of the source of oxygen and nitrogen ($O_2$, $N_2$, or $NO_2$).

Practically, this was done as follows. The unsensitized mixture [Eq. (1)] was prepared by selecting a certain nitrogen dilution, labeled $\beta$. The equivalent sensitized mixture [Eq. (2)] was then prepared by first selecting the amount of $NO_2$ desired. This fixes parameter $c$. The amounts of $O_2$ and $N_2$ (parameters $a$ and $b$) were then adjusted to achieve the same dilution as in Eq. (1). The required relations for $a$ and $b$ are given in Eq. (3):

$$C_3H_8 + 5(1O_2 + \beta N_2) \rightarrow 4H_2O + 3CO_2 + 5\beta(N_2), \quad (1)$$

$$C_3H_8 + 5(aO_2 + bN_2 + cNO_2) \rightarrow 4H_2O + 3CO_2 + 5\beta(N_2), \quad (2)$$

$$a = 1 - c, \qquad b = \beta - c/2. \quad (3)$$

The concentration of $NO_2$ was varied from a 0.1 to a 0.5 ratio of $NO_2$ to fuel:

$$0.1 \leqslant \frac{P_{NO_2}}{P_{C_3H_8}} \leqslant 0.5. \quad (4)$$

The nitrogen dilution was varied from 0.0 (i.e., no nitrogen dilution) to 3.76 (nitrogen-to-oxygen ratio in standard air).

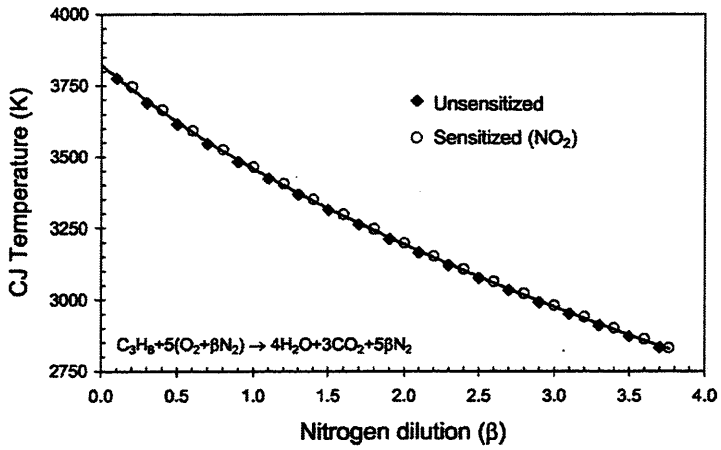


Fig. 2. Effect of $NO_2$ on the CJ temperature.

In order to confirm that these two mixtures [Eqs. (1) and (2)] have the same energetics, the CJ detonation temperature was calculated using the NASA Chemical Equilibrium with Applications (CEA) code [17] for both mixtures over the range of nitrogen dilution tested and for the maximum addition of $NO_2$. The results are presented in Fig. 2. From this graph, we clearly see that the CJ temperature for mixtures sensitized with $NO_2$ is nearly the same as that of the mixtures without $NO_2$. Similar results are obtained in comparing equilibrium detonation velocity for the sensitized and unsensitized mixtures; no difference is observed. The fact that all the points lie on the same curve indicates that the energy release is the same for a given nitrogen dilution. In other words, the method of mixture comparison outlined above effectively eliminates the potential energetic effect of $NO_2$ and allows us to isolate its sensitizing effect on DDT and cell size in $C_3H_8$– $O_2$– $N_2$– $NO_2$ mixtures.

A final concern is the fact that gaseous nitrogen dioxide is actually an equilibrium composition of $NO_2$ and $N_2O_4$. The equilibrium concentration is a function of temperature and partial pressure. The equilibrium fraction of $NO_2$ was calculated using CEA [17] for a range of temperatures and pressures. The results indicate that for a partial pressure around 0.01 bar and 21 °C (typical of all the experiments) the gas composition is approximately 90% $NO_2$ and 10% $N_2O_4$. Therefore, Eq. (2) becomes

$$C_3H_8 + 5[aO_2 + bN_2 + c'(0.9NO_2 + 0.1N_2O_4)] \rightarrow 4H_2O + 3CO_2 + 5\beta(N_2), \quad (5)$$

$$c' = c/1.1. \quad (6)$$

Now, $c$ is the amount of $NO_2$ desired, as stated in Eq. (2), and $c'$ corresponds to the actual amount of gas injected with respect to the other constituents. In the following sections, when referring to $NO_2$, it is understood that the equilibrium composition of $NO_2/N_2O_4$ described above actually exists.

Experiments were first performed for mixtures of $C_3H_8$– $O_2$– $N_2$ over the full range of nitrogen dilution to establish a baseline for run-up distance and cell width. The effect of $NO_2$ addition was then evaluated by comparing run-up distance and cell width over the same range of nitrogen dilution with varying concentrations of $NO_2$.

## 3. Results and discussion

### 3.1. Run-up distance without chemical additives

Experiments were performed initially for the stoichiometric mixtures represented by Eq. (1). The run-up distance to detonation was determined from the velocity profile of the combustion wave as it traveled down the tube. A typical result for a value of $\beta = 3.1$ is presented in Fig. 3, which shows the velocity of the combustion wave vs the distance along the tube. Each data point corresponds to the average velocity between adjacent ionization probes. The upper dashed line indicates the theoretical Chapman–Jouguet detonation velocity for this mixture, which was calculated using the NASA CEA code [17]. The lower dashed line indicates the experimental detonation velocity observed, which is simply the average velocity after the wave reaches steady state. The large velocity deficit due to the effect of the obstacles has been observed and described by numerous researchers [18–20] in studying the propagation of detonations in rough tubes.

We can see from Fig. 3 that the combustion wave quickly accelerates to a high-speed (supersonic) turbulent deflagration. The run-up distance, labeled

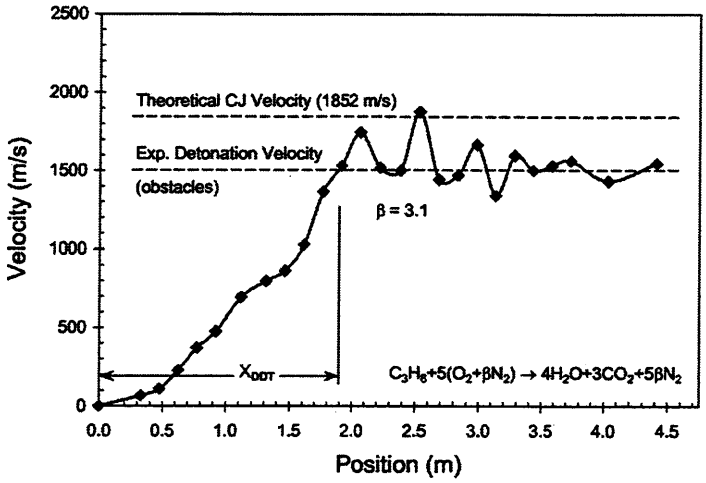


Fig. 3. Typical velocity profiles for $C_3H_8$–$O_2$–$N_2$.

$X_{DDT}$, is the distance from the igniter to the location where the wave first reaches the detonation velocity. In this case the run-up distance is ~ 1.9 m. Despite the complex nature of DDT, the results were very reproducible for a given mixture. The largest fluctuations in run-up distance observed were ±1 tube diameter.

### 3.2. *Run-up distance with $NO_2$*

Experiments were performed for the stoichiometric mixtures represented by Eq. (2) [or Eq. (5)]. Typical velocity profiles are presented in Fig. 4 for sensitized and unsensitized mixtures at two levels of nitrogen dilution, corresponding to $\beta = 1.0$ and $\beta = 3.1$. In both cases, the $NO_2$ addition is the maximum tested [$NO_2$-to-fuel ratio 0.5 or, equivalently, $c = 0.1$ in Eq. (2)]. In terms of using $NO_2$ as a fuel additive, this is a very significant amount, corresponding to a sensitized "fuel" composed of 33% $NO_2$. We note from Fig. 4 that the run-up distance is unaffected by the $NO_2$ addition as long as the fuel-to-oxidizer and oxidizer-to-diluent ratios are kept constant. The apparent variation for the high-$\beta$ case corresponds to about 1 tube diameter and is within the scatter of the results.

A summary of all the run-up distance measurements for mixtures with and without $NO_2$ is presented in Fig. 5, which shows the run-up distance vs nitrogen dilution ($\beta$) for over 100 shots (repeated results are overlaid). Different symbols are used to represent the unsensitized mixtures and the various $NO_2$ concentrations. A trend line has been added through the unsensitized data points. The tight grouping of the data around the trend line confirms the reproducibility of the results. As expected, the run-up distance increases

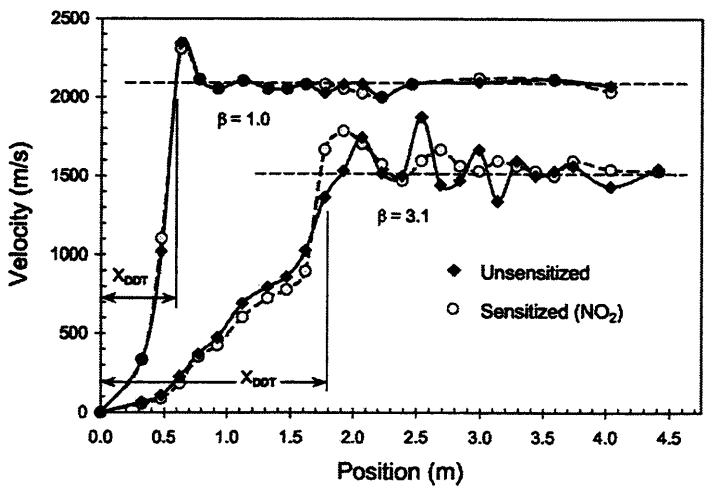


Fig. 4. Effect of $NO_2$ on the velocity profile.

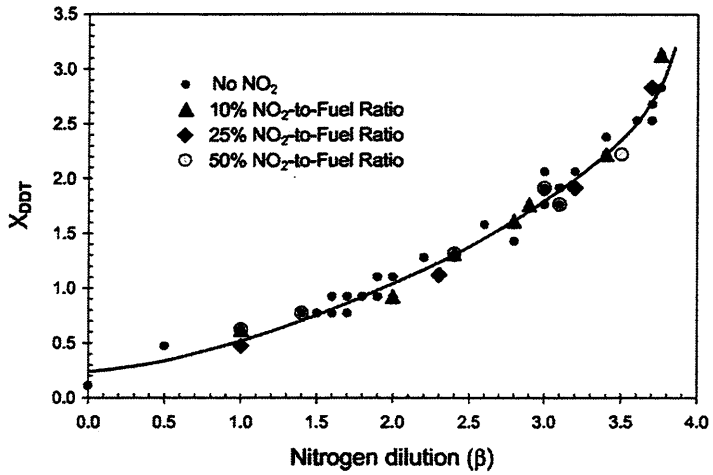


Fig. 5. Effect of $NO_2$ on run-up distance.

as the nitrogen dilution is increased, ranging from 0.1 m for propane–oxygen to 3 m for propane–air. If we focus on any given value of nitrogen dilution, we see that there is no change in run-up distance as $NO_2$ is added. This is true for the whole range tested: all the points lie along the same trend line. In none of the cases has $NO_2$ sensitized the mixture. This implies that $NO_2$ simply acts as an oxidizing agent, equivalent to the $O_2$ it replaces. In other words, its effect is purely energetic.

### 3.3. *Effect on cell size*

In order to confirm the run-up distance data obtained, the detonation cell size was measured. Data were collected for $\beta = 1.0$, 1.4, 2.4, and 3.0 without $NO_2$ and with the $NO_2$-to-fuel ratio 0.5 (i.e., the highest additive content tested). Figure 6 shows average cell size in millimeters as a function of percentage of nitrogen in the total mixture with pictures of two of the experimental results overlaid. The percentage of nitrogen was selected rather than the nitrogen dilution in order to improve the linear fit with respect to the logarithm of the cell width. They are related by

$$\%\,N_2 = \frac{5\beta}{1+5(1+\beta)} \times 100. \tag{7}$$

The equations for determining the $NO_2$ mixtures with the same nitrogen dilution (therefore the same % $N_2$) as mixtures without $NO_2$ are described in the

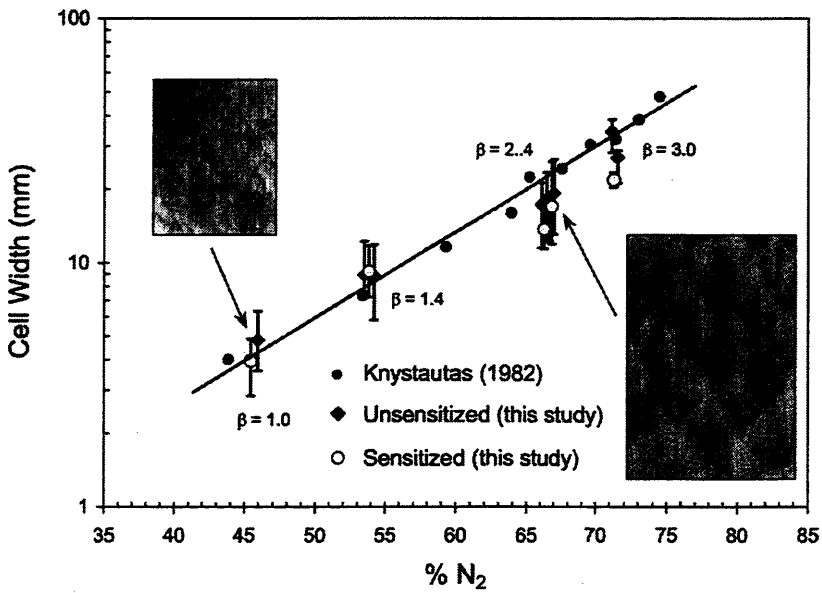


Fig. 6. Effect of $NO_2$ on cell size.

previous section. Data from Knystautas et al. [21] for $C_3H_8$–$O_2$–$N_2$ mixtures along with an exponential fit are presented for reference. A number of experiments were done at each value of $\beta$, and the data have been spread out only to help in visualizing the data points and error bars.

The measured cell sizes correspond quite well with those of Knystautas et al. [21], especially at lower values of nitrogen dilution. As the nitrogen dilution increases, the cells become more irregular and fewer cells can "fit" across the tube, making the appropriate cell size more difficult to determine. It is particularly important to note that all the cell sizes in mixtures with $NO_2$ addition fall within the error bars of the mixtures without additive. This confirms the conclusions of the previous section, i.e., that $NO_2$ has no sensitizing effect on these mixtures.

The results presented clearly indicate that $NO_2$ does not have an effect on DDT or cell size for $C_3H_8$–$O_2$–$N_2$ mixtures. This appears to be in contradiction with results indicating significant reductions in induction time for both diesel fuels [1,2] and hydrocarbon fuels [4,5] with very small amounts of nitrate compounds or $NO_2$. On the other hand, it is not in contradiction to the detonation studies presented earlier [7,8], in which significant amounts of additive were required to effect changes in sensitivity. There appears to be a fundamental difference between the former results based on induction time measurements and the latter detonation sensitivity measurements. The results of Tieszen et al. [9] described above indicate, as does this study, that the $NO_2$ itself is not sufficient for detonation sensitization.

In order to resolve this issue, the path for sensitization and its dependence on temperature must be examined. Indeed, the post-shock temperature in a detonation ($\sim$ 1600 K) is generally higher than the temperature at which additives showed a significant effect on the induction time. When these studies evaluated a temperature range, the effectiveness of the additives decreased with increasing temperature. Two proposed mechanisms [10,22] for $NO_2$ sensitization will be presented in order to illustrate the need for a feedback loop that maintains the $NO_2$ concentration and allows for a catalytic effect, and the effect of ignition temperature on the loop mechanism.

Slutskii [10] suggests that $NO_2$ reduces induction time by leading to a $CH_3$ oxidation channel:

$$\begin{aligned} &CH_3 + NO_2 \rightarrow NO + CH_3O, \\ &NO + HO_2 \rightarrow NO_2 + OH. \end{aligned} \tag{8}$$

$CH_3$ radicals are present in the oxidation reactions of all hydrocarbons and tend to inhibit high-temperature ignition by recombining, resulting in chain termination [23]:

$$CH_3 + CH_3 \rightarrow C_2H_6. \tag{9}$$

A rapid oxidation path for $CH_3$ should therefore accelerate ignition kinetics, which should in turn reduce the characteristic detonation length scales. A more recent model resulting from the study of nitrate promoters in diesel fuel [22] suggests the following paths for $NO_2$ sensitization:

$$\begin{aligned} &NO_2 + RH \rightarrow HONO + R, \\ &HONO \rightarrow NO + OH, \\ &2NO + O_2 \rightarrow 2NO_2, \end{aligned} \tag{10}$$

and

$$\begin{aligned} &NO_2 + RH \rightarrow HNO_2 + R, \\ &O_2 + HNO_2 \rightarrow HO_2 + NO_2, \end{aligned} \tag{11}$$

where R is a fuel radical.

In both of these models, a species is required (either the $HO_2$ radical or $O_2$) to "regenerate" $NO_2$ thus allowing it to act as a *catalyzer* for ignition. Indeed, if trace amounts of additive are to play a major role, the effect should be catalytic, so that it may affect a significant number of elementary reactions without being rapidly consumed [24].

Slutskii [10] explains that the reactions that create $HO_2$ at lower temperature,

$$\begin{aligned} &CHO + O_2 \rightarrow CO + HO_2, \\ &\quad k = 3.4 \times 10^{12}, \quad \text{and} \\ &CH_3O + O_2 \rightarrow CH_2O + HO_2, \\ &\quad k = 10^{12} \exp(-2250/T), \end{aligned} \tag{12}$$

are replaced by another set of reactions which become more rapid at higher temperature (> 1100–1200 K),

$$\begin{aligned} &HCO + M \rightarrow H + CO + M, \\ &\quad k = 5.5 \times 10^{14} \exp(-8900/T), \quad \text{and} \\ &CH_3O + M \rightarrow CH_2O + H + M, \\ &\quad k = 5 \times 10^{13} \exp(-10{,}000/T), \end{aligned} \tag{13}$$

where $k$ is the forward rate for each reaction and M is a nonreacting species. The dependence of the rate constants on temperature, according to the standard Arrhenius form, causes the switchover from reactions (12) to reactions (13) at the higher temperature ignition characteristic of a detonation. It is possible that the $O_2$ required in the second model proposed (developed for diesel fuel ignition below 1000 K) is likewise not available at higher temperatures. The high-temperature ignition typical of a detonation would therefore not benefit substantially from

the presence of $NO_2$, which would be consumed very rapidly. In another example, Dorko et al. [25] demonstrated important reductions in ignition delay of $CH_4$–$O_2$ when part of the $O_2$ was replaced with $NO_2$; however, the reduction in the induction time is indeed less pronounced at higher temperatures. If this were the case, the small amount of $NO_2$ present in our experiments would be consumed in a negligibly small number of reactions, leading to an indistinguishable effect on the ignition kinetics, which would explain the lack of effect of $NO_2$ on run-up distance and cell size.

In order to verify the assumptions made above, simulated ignition experiments should be performed with a mechanism accounting for the kinetics of $C_3$ and lower hydrocarbons and for $NO_2$ kinetics at temperatures ranging from 1000 to 1600 K. It is expected that the difference in ignition delay should decrease as the temperature increases. This should be reflected in a progressively more rapid depletion of $NO_2$ with increasing ignition temperature.

## 4. Conclusions

The effect of $NO_2$ on the detonation sensitivity of propane has been studied experimentally. The objective was to establish whether a small quantity of additive could sufficiently alter the kinetics of hydrocarbon–$O_2$–$N_2$ mixtures to affect their detonability. Previous investigations showing significant reductions in induction delay of diesel and hydrocarbon fuels with varying amounts of nitrate sensitizers indicated a promising route. Analysis of the results obtained with nitrates has allowed previous researchers to identify a path to sensitization dominated by the catalytic effect of $NO_2$ on the ignition kinetics of the fuel. More recent studies on the effect of nitrate sensitizers on the detonation characteristics of hydrocarbon fuels have indicated some effectiveness, but typically requiring a large amount of additive. This has made it difficult to evaluate the effectiveness of these compounds as sensitizers.

This study has presented a method for comparing the sensitivity of fuel–$O_2$–$N_2$ mixtures with and without $NO_2$ in such a way as to isolate the kinetic effects by eliminating energetic differences in the mixtures. The experiments were carried out with mixtures of $C_3H_8$–$O_2$–$N_2$, with $NO_2$ concentrations varying from 10 to 50% of the fuel concentration. Mixtures with identical energetics invariably displayed identical sensitivity as established by comparing run-up distance and cell size, indicating that the $NO_2$ additive is not resulting in significant kinetic effects. This apparent contradiction to the previous work appears to be due to the temperature difference between typical diesel ignition studies and detonations. Reactions required to maintain the $NO_2$ concentration are not present at higher temperatures (above 1100–1200 K), thus the catalytic effect of $NO_2$ is eliminated. By this reasoning, nitrate compounds cannot be considered as sensitizers for hydrocarbon–air detonations.

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## Appendix 4: Effect of Peroxide Additives on the Detonation Sensitivity of Hydrocarbon Fuels

**Reprint of:** Landry D., McIntosh S., and Higgins, A.J., "Effect of Peroxide Additives on the Detonation Sensitivity of Hydrocarbon Fuels," AIAA-2003-5203, 39th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, Huntsville, Alabama, July 2003.

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# Effect of Peroxide Additives on the Detonation Sensitivity of Hydrocarbon Fuels

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# Effect of Peroxide Additives on the Detonation Sensitivity of Hydrocarbon Fuels

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**Abstract**

The effect of peroxides on the detonation sensitivity of a representative hydrocarbon fuel is experimentally investigated. The peroxides (tert-butyl hydroperoxide and hydrogen peroxide in water solution) were added to decane fuel in vapor form. The fuel/oxygen mixtures were prepared at elevated temperatures and injected into a heated detonation tube at temperatures between 150 – 250 °C and at pressures of 7.6 – 9 kPa. The mixtures were spark ignited and the distance required for the flame to accelerate to a detonation was measured via fiber optics. The results show that the addition of these peroxides does not result in a reduction in the run up distance to detonation. As the concentration of the peroxides is increased, the run up distance increases, indicating a reduction in sensitivity. The addition of tert-butyl hydroperoxide results in a shift of the maximum sensitivity to very fuel rich conditions.

## 1. Introduction

The present paper reports an investigation of the sensitizing effect of peroxide additives in a hydrocarbon/oxygen mixture. A mixture is said to be sensitive to detonation when it is easily detonated. Traditional methods of evaluating detonation sensitivity consist of measuring the detonation cell sizes, the critical diameter or the energy required to directly initiate a detonation in the mixture. However, it is possible to qualitatively assess the relative detonation sensitivity of various mixtures by determining their respective deflagration to detonation transition (DDT) run-up distances. Although no quantitative relationship has yet been established relating cell sizes to run-up distances, the latter method provides a qualitative as well as a self-consistent measurement of detonation sensitivity.

In a recent study, Romano et al. [1] demonstrated experimentally that when a pentane/oxygen mixture is ignited during a partial oxidation, referred to as a "cool flame" process, its run-up distance significantly decreases. The "cool flame" process is characterized by the production of aldehydes originating from the partial oxidation of the hydrocarbon fuel. The process then evolves to generate peroxides and other free radicals which create the characteristic chemiluminescence sometimes visible. No significant exothermicity is observed however, and the mixture only increases in temperature on the order of 150°C. As demonstrated by Romano et al. [1], if the mixture is ignited during this process, the run up distance to detonation can be reduced by as much as 50% compared to its value prior to the cool flame.

The present work is directed toward determining if a sensitization effect, similar to the cool flame effect, can be realized via peroxide addition to hydrocarbon/oxygen mixtures. Several peroxides are of interest in this ongoing study. Tert-butyl hydroperoxide (TBHP, $(CH_3)_3COOH$) is representative of the peroxide species present in the "cool flame" effect and thus may be responsible for the observed decrease in the run-up distance. In another instance, very promising numerical computations have been carried out for mixtures containing hydrogen peroxide ($H_2O_2$). In the study of Frolov et al. [2], the effect of adding hydrogen peroxide to iso-octane ($C_8H_{18}$) was studied via chemical kinetic calculations. They found that the addition of 20% and 60% hydrogen peroxide by mole of $O_2$ resulted in a decrease in cell size of the order of approximately 10

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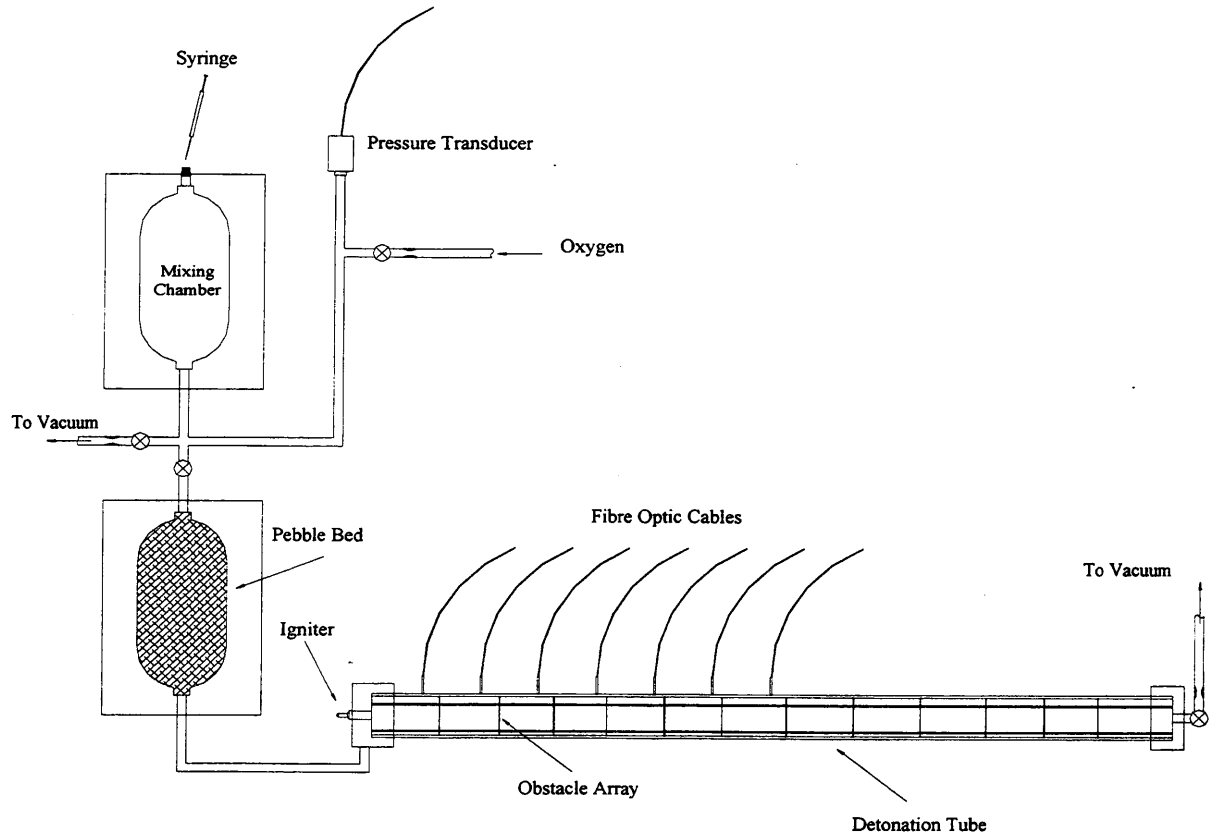


Figure 1. Experimental Set-up

and 100 times, respectively. Another numerical study performed with chemical kinetics mechanisms by Catoire et al. [3] showed that hydrogen peroxide added in small amounts (from 1% to 5% by mole of oxygen) to stoichiometric mixtures of n-heptane/air and n-decane/air significantly decreased (by a maximum factor of 2.6) the ignition delays for a temperature range of 700-1250 K and pressure range of 12-50 bars.

The current interest in pulse detonation engines (PDE) provides renewed enthusiasm in determining methods of reducing transition from deflagration to detonation in otherwise insensitive heavy hydrocarbons. The ability to chemically sensitize a hydrocarbon fuel, in effect artificially accelerating the rate of chemical reaction, may have other important applications to high-speed air breathing propulsion, such as scramjets.

Thus, the objective of the present study is to investigate the effect of peroxide addition on the detonation sensitivity of heavy hydrocarbon/oxygen mixtures via measurement of run-up distances. The fuel used in this investigation is decane ($C_{10}H_{22}$) and the peroxides used are hydrogen peroxide ($H_2O_2$) and tert-butyl hydroperoxide ( $(CH_3)_3COOH$ ). Decane is used as a representative heavy hydrocarbon fuel with a low vapor pressure, similar to fuels of interest for pulse detonation engines and other air-breathing propulsion concepts.

## 2. Experimental Details

### 2.1 Apparatus

In order to investigate the effect of peroxide addition on the sensitization to DDT of a hydrocarbon/oxygen mixture, the combustible mixture was prepared via partial pressures at elevated temperatures to ensure that the components remained in the vapor phase, but below temperatures where auto-ignition or ratio partial oxidation and cool flames occur. Subsequently, the mixture was injected into a heated detonation tube where it was ignited by a weak spark, which gave rise to a deflagration. As the deflagration accelerated, it eventually reached a point where a transition to a

detonation (DDT) occurred within the detonation tube length. Hence, the sensitizing effect of the additives was determined by obtaining the resulting run-up distances and comparing them to those obtained in absence of the additives.

The mixtures were prepared inside a 1 liter stainless steel cylindrical vessel, maintained at a temperature of 150°C by two semi-circular Watlow ceramic heaters each rated 900 W at 120 V, with a surface loading of 13.6 W/cm$^2$. The pressure in the apparatus was monitored by a pressure transducer (Omegadyne part no. PX02C1-025AV) rated for 0-25 psia at a maximum operating temperature of 163°C. A pressure snubber (Omega part no. PS-4G) was positioned between the pressure transducer's port and the apparatus assembly in order to protect the transducer in the event of pressure spikes (which would occur if the mixture were to auto-ignite in the mixing chamber). Since the liquid fuel used (n-decane) can potentially condense on the surface of the transducer membrane, the oxygen was added prior to the fuel in order to provide a gas barrier between the mixing chamber and the pressure transducer. The liquid fuel was injected inside the mixing chamber using a syringe through a small rubber stopper. The amount of liquid injected was calculated using the known density of the liquid, and the resulting pressure increase monitored by the pressure transducer confirmed the fuel was completely vaporized.

Once the desired mixture was obtained in the mixing chamber, a solenoid valve was opened which allowed the mixture to flow through a heated pebble bed subsequently filling the detonation tube. The time required to reach the final pressure inside the detonation tube was measured to be approximately 4 seconds.

The pebble bed was maintained at the same temperature as the tube, and the large surface area of the beads ensured the gas was heated to nearly the desired temperature as it flowed into the tube. As a result, temperature gradients inside the heated detonation tube were minimized. The pebble bed consisted of a 1 liter stainless steel cylindrical vessel filled with 6.3 mm-diameter steel spheres. Once again, heating was provided by two semi-circular Watlow ceramic heaters each rated 900 W at 120 V with a surface loading of 13.6 W/cm$^2$.

The heated detonation tube was a 1.23 m long heavy wall Pyrex tube with a 57.1 mm outside diameter (Dow Corning catalog no. 237570). Heating was provided by six ultra-high temperature heating tapes, each rated 627 W at 120 V with a surface loading of 13 W/in$^2$ (Omega STH101-040), longitudinally positioned along the detonation tube. In order to maintain the heating tapes in close contact with the surface of the tube, they were enclosed in a tubular fiberglass insulation, fixed around the tube with metallic hose clamps. The insulation was fixed so that the heating tapes as well as the thermocouple could easily be accessed.

An obstacle array, consisting of successive rings of wire (2 mm diameter) spaced 1 diameter apart from each other, was used in order to promote acceleration in the initial laminar to turbulent flame transition. Additionally, the obstacles' presence reduced the shot-to-shot variability of the transition distance to within one tube diameter. Hence, the regime prior to detonation focused principally on the fast turbulent deflagration and transition to detonation instead of the laminar and weak turbulent flame, where the sensitization by radicals is thought to have a negligible effect [1].

A delay of 3 seconds was allowed after the closing of the solenoid valve in order to ensure that the mixture had completely filled the detonation tube. The mixture was then ignited by a weak spark generated by an EG&G TM-11 trigger module capable of discharging about 30 mJ at 30 kV through a Champion RC12LYC spark plug.

The acceleration of the flame and its transition to detonation were recorded using a series of fiber optic cables positioned along the length of the detonation tube at predetermined distances. The optic signal from the fibers was converted to a voltage signal using photo-diodes. The run-up distance could then be determined with an accuracy of approximately 2 cm (~½ tube diameter).

The entire apparatus temperature was monitored by K-type thermocouples mounted between each heater and the surface which they contact, thus permitting each heater to be monitored and adjusted individually*. The adjustment of the temperature was provided by a National Instruments LabView interface which regulated the power output of the various heaters through solid state relays. A steady and uniform temperature could be maintained throughout the entire

* The only exception is the detonation tube, where one thermocouple controls the six tape heaters.

evacuated apparatus to within ±5°C, over a range 20-250°C.

In order to ensure that the fuel remained in gaseous form in the entire apparatus, the following test was performed. The entire apparatus was brought to a uniform temperature of 150°C. The mixing chamber was then filled with oxygen to a given pressure, the solenoid valve connecting the mixing chamber to the pebble bed and detonation tube was then opened, allowing the oxygen to fill the entire apparatus. Once the pressure stabilized, its value was noted and the ratio of the final pressure over the initial pressure was determined. This procedure was then repeated using a fuel-rich (equivalence ratio $\Phi \sim 2.5$) mixture of decane-oxygen. The ratios were subsequently compared and were found to be the same, thus ensuring that the apparatus was heated appropriately such that no fuel condensation occurred.

All experiments were conducted using a pressure of 27.6 kPa psia inside the mixing chamber. This resulted in a pressure of 7.6 kPa inside the detonation tube at 150°C, 8.3 kPa at 200°C and 9.0 kPa at 250°C.

The peroxides and fuel used were obtained from Sigma-Aldrich. Since the tert-butyl hydroperoxide was available in a prepared solution in decane (catalog no. 41,666-5), the desired concentrations were easily achieved by dilution with pure decane (catalog no. D90-1). Hydrogen peroxide was obtained as a 50% by weight in water solution (catalog no. 51,681-3). Since hydrogen peroxide and water are not miscible in decane, the desired mixture concentrations were obtained directly in the mixing chamber using the method of partial pressures. The procedure consisted in filling the mixing chamber with the appropriate amount of oxygen, then the hydrogen peroxide solution was added, followed by the addition of decane.

## 2.2 Mixture Preparation

In order to avoid confusion as to the concentrations of fuels and additives of the various mixtures, an outline of the procedure employed to derive the composition of the mixtures is given here.

The mixture of decane oxygen is given below in its balanced stoichiometric form:

$$C_{10}H_{22} + 15.5\,O_2 \rightarrow 10\,CO_2 + 11\,H_2O$$

The equivalence ratio, $\phi$, is given by the ratio of fuel to air of the mixture over the stoichiometric ratio of fuel to air:

$$\phi = \frac{(FA)}{(FA)_{stoichiometric}}$$

The partial pressures required to obtain the desired mixtures are thus easily computed. Applying the ideal gas law, the partial pressures are given by the mole fractions of the various reactants. Hence, knowing the desired pressure in the mixing chamber to be 27.6 kPa, the partial pressure of the fuel is:

$$\left(\frac{\phi}{15.5+\phi}\right) 27.6\ kPa$$

and the partial pressure of oxygen is:

$$\left(\frac{15.5}{15.5+\phi}\right) 27.6\ kPa\,.$$

In a similar fashion, the equations of the other mixtures containing the different peroxides are obtained. For the tert-butyl hydroperoxide/decane/oxygen, the stoichiometric equation used is:

$$C_{10}H_{22} + \beta\, C_4H_{10}O_2 + (5.5\,\beta + 15.5)\,O_2 \rightarrow (10+4\beta)CO_2 + (11+5\beta)H_2O$$

where β is the percentage concentration, by mole, of TBHP with respect to decane.

For the (hydrogen peroxide-water solution[1])/decane/oxygen mixtures:

$$C_{10}H_{22} + \gamma(1.888H_2O + H_2O_2) + (15.5 - \gamma/2)O_2 \rightarrow 10CO_2 + (11 + 2.888\gamma)H_2O$$

where γ is the percentage concentration, by mole, of HP with respect to decane.

As an indication, some partial pressures for various mixtures (at a mixing chamber pressure of 27.6kPa) are listed in Table 1.

[1] 50% $H_2O_2$ in $H_2O$, by weight.

Table 1. Partial Pressure for Mixtures

| Equivalence Ratio (ϕ) | Partial Pressure (kPa) | Decane-Oxygen | Decane-30%TBHP-Oxygen | Decane-10%HP in solution-Oxygen |
|---|---|---|---|---|
| 0.6 | Fuel | 1.03 | 1.20 | 1.32 |
| | Oxygen | 26.57 | 26.40 | 26.28 |
| 1.0 | Fuel | 1.67 | 1.94 | 2.13 |
| | Oxygen | 25.93 | 25.66 | 25.47 |
| 1.2 | Fuel | 1.98 | 2.30 | 2.51 |
| | Oxygen | 25.62 | 25.30 | 25.09 |
| 2.0 | Fuel | 3.15 | 3.630 | 3.95 |
| | Oxygen | 24.45 | 23.97 | 23.65 |

The concentration of peroxide additive is given with respect to the fuel used and is included in the fuel's partial pressure.

## 3. Results

### 3.1 Evaluation of the Run-Up Distances

The mixtures were ignited at one end of the detonation tube by a spark plug. From previous studies [4,5,6], it is known that a flame will accelerate very rapidly in an obstacle field after ignition. When the turbulent flame reaches a speed at which shock-induced reactions occur, detonation initiation may occur. The initiation is usually associated with localized pockets of gas which explode to form a detonation wave [7,9]. The detonation wave is initially overdriven, but quickly decays to the Chapman-Jouguet (CJ) detonation velocity. The distance from the location of the spark to the onset of detonation is referred to as the run-up distance. As can be observed from Figure 2, this distance is very reproducible for identical mixtures in the same apparatus.

The velocity profiles for all the mixtures studied exhibit the same behavior as in Figure 2.

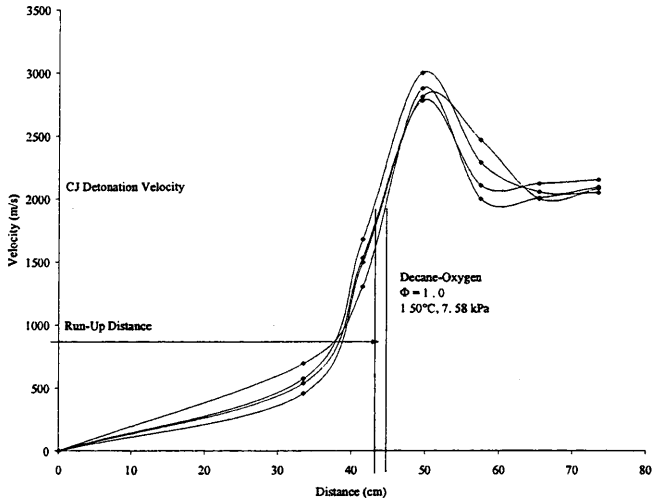


Figure 2. Typical Flame/Detonation Velocity Profiles

### 3.2 TBHP Addition to Decane/Oxygen Mixtures

The run-up distances for decane/TBHP/oxygen mixtures of different concentrations at an equivalence ratio of 1 were obtained and are shown in Figure 3.

Stoichiometric mixtures of decane/TBHP/oxygen exhibit an increase in the run-up distance as the concentration of TBHP increases. At elevated concentrations (higher than 30% TBHP by mole with respect to decane at 150°C and 200°C, and higher than 20% at 250°C), the mixture cannot be ignited with the ignition system used.

The effect of the variation of the equivalence ratio of the mixtures was investigated at temperatures of 150°C and 200°C. It was observed that as the concentration of TBHP increased, it was possible to obtain a detonation at higher equivalence ratios. As shown in Figures 4 and 5, the minimum run-up distances thus obtained were of the same order as those obtained for decane/oxygen mixtures.

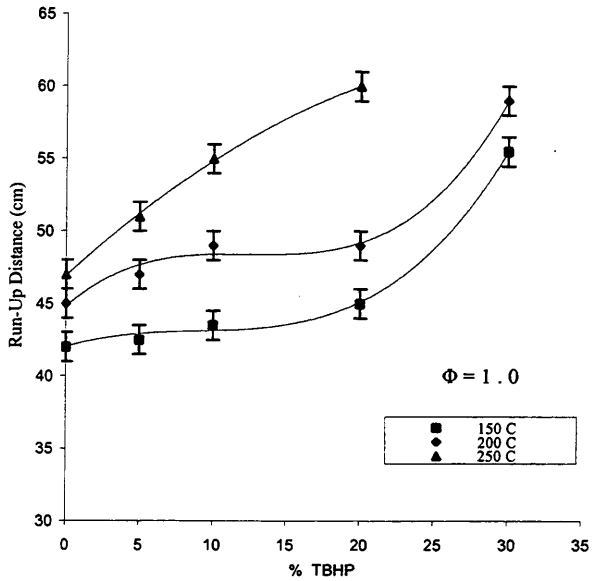


Figure 3. Run-Up Distances for Various Concentrations of TBHP

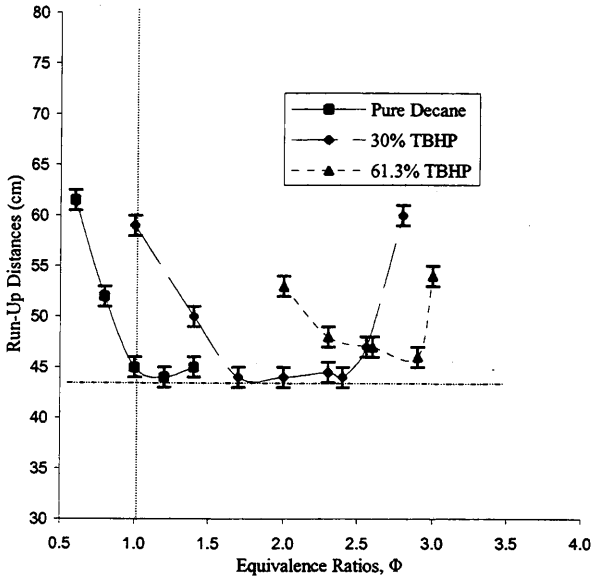


Figure 5. Equivalence Ratio Dependence at 200°C

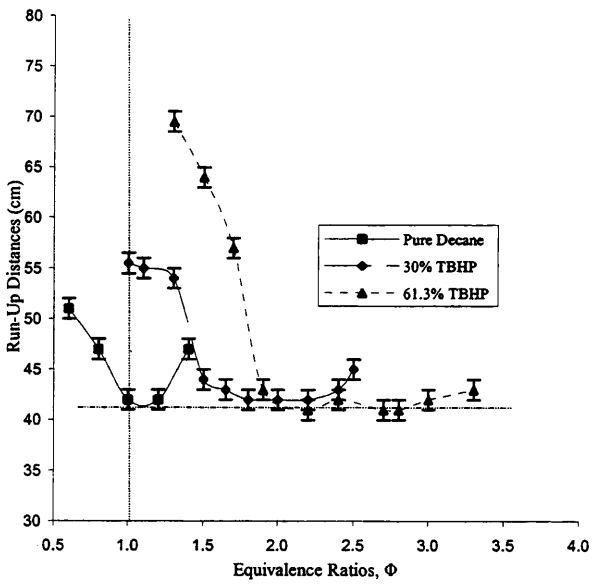


Figure 4. Equivalence Ratio Dependence at 150°C

Detonation cell size measurements were obtained for mixtures of 0% ($\Phi$ = 1.25), 30% ($\Phi$ = 2.0) and 61.3% ($\Phi$ = 2.5) addition of TBHP. The equivalence ratios of the mixtures were chosen to correspond to mixture compositions which exhibited the minimum run-up distance of 42 cm. All measurements were performed for initial mixture temperature of 150°C. The cell sizes were found to be 8.3 mm ± 2 mm for all mixtures. This observation was consistent with the fact that the run-up distances were similar for all these mixtures.

### 3.3 HP Solution Addition to Decane/Oxygen Mixtures

Run-up distances were determined for stoichiometric mixtures of HP solution in decane/oxygen mixtures. The solution utilized consisted of a mixture of 50% HP in water by weight. This implied that for each mole of HP there was 1.888 moles of water. Hence, the mixtures studied had water concentrations of almost twice as that of the HP.

Figure 6 shows the effect of addition of the HP solution on the run-up distance of decane/oxygen mixtures. As the amount of HP solution increases, the run-up distance increased.

Since the mixtures used contained high concentrations of water, experiments were performed with water as an additive to decane/oxygen mixtures at 150°C. Figure 6 also shows the run-up distances obtained for various concentrations of water. In order to compare the effect of having HP as an additive, the results for water experiments were plotted against the corresponding HP concentrations, where the concentration of water (with respect to decane) contained in the mixture is the same.

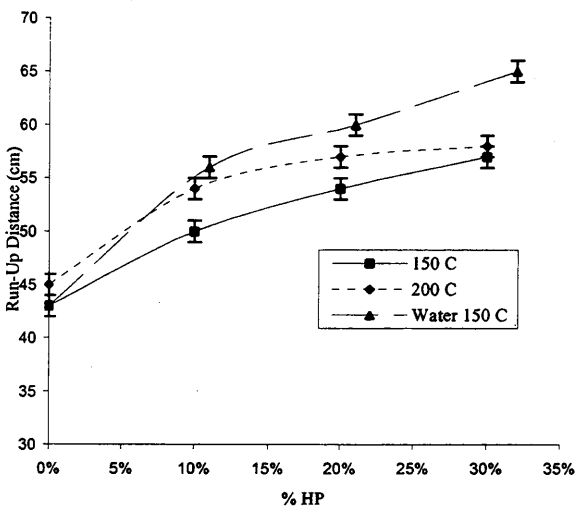


Figure 6. Run-Up Distances for Various HP Concentrations

## 4. Discussion of Results

### 4.1 Effect of TBHP addition

The presence of tert-butyl hydroperoxide increases the run-up distance if the mixture's equivalence ratio is fixed. For increasing concentrations of TBHP, the run up distance increases accordingly. Furthermore, as the temperature increases, the inhibiting effect of TBHP becomes more important. Eventually, if the temperature or concentration is too elevated, the mixture cannot be ignited.

It is possible to recover the shortest run-up distance in the presence of TBHP in the mixture by increasing the equivalence ratio, which is achieved by diminishing the amount of oxygen introduced in the mixture. This may be caused by the strong oxidizing behavior of TBHP. Additionally, the plateau where the run-up distance is minimal over some equivalence ratios is increased significantly in the presence of TBHP at concentrations of 20% and more.

The presence of TBHP in a mixture of decane/oxygen does not, however, decrease run-up distance in any significant manner. This observation suggests that the effect observed by Romano et al [1] is not due to the presence of TBHP during cool flame. Furthermore, cell size measurements of mixtures of TBHP/decane/oxygen at 200°C show similar results; the sensitivity of the mixture is unaltered by the presence of TBHP (if the equivalence ratio is set such that the minimum run-up distance is obtained).

### 4.2 Effect of HP solution addition

The addition of hydrogen peroxide, in an aqueous solution at concentrations of 50% by weight, to decane/oxygen mixtures resulted in an increase in run-up distances. As concentrations of HP and temperatures increased, the run-up distances also increased. Control experiments in which just water was added showed a greater increase in run-up distance. Thus, the presence of HP has a sensitizing effect over just water alone. However, this sensitizing effect is not able to overcome the diluting effect of the water when HP is added as a 50% solution by weight.

## 5. Conclusions

The presence of tert-butyl hydroperoxyde in mixtures of decane/oxygen at various equivalence ratios was shown to not significantly sensitize the detonation sensitivity of decane. Its presence at elevated concentrations required the mixture to be oxygen deficient in order to obtain the minimum run-up distance; TBHP addition shifted the maximum sensitivity to fuel rich mixtures.

Hydrogen peroxide at a concentration of 50% by weight in an aqueous solution was shown to lengthen run-up distances in decane/oxygen mixtures. Experiments conducted with water as an additive revealed that the presence of water lengthens run-up distances. When HP was added to decane/water/oxygen mixtures, the run-up distances decreased in comparison to the comparable water addition, but did not result in a more sensitive mixture in comparison to pure decane.

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## Appendix 5: Sensitization of Pentane-Oxygen Mixtures to DDT via Cool Flame Oxidation

**Reprint of:** Romano, M.P., Radulescu, M.I., Higgins, A.J., and Lee, J.H.S., "Sensitization of Pentane-Oxygen Mixtures to DDT via Cool Flame Oxidation," *Combustion and Flame,* Vol. 132, *2003,* pp. *387-394.*

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# Sensitization of pentane-oxygen mixtures to DDT via cool flame oxidation

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**Abstract**

The effect of cool flame partial oxidation on the detonation sensitivity of a hydrocarbon fuel was investigated experimentally. The detonation sensitivity was quantified by measuring the run-up distance required for a deflagration to transit to a detonation wave (DDT) in a rough tube. Fuel rich pentane-oxygen mixtures at sub-atmospheric initial pressures were studied. Subsequent to the injection of the mixture into a heated detonation tube, the mixture underwent cool flame oxidation after a well-controlled delay time, dependent on the temperature of the tube. Typical delays ranged from 0.5 to 2 s (depending on temperature) and were reproducible to within one hundred milliseconds. This delay permitted the mixture in the detonation tube to be spark-ignited at various stages of the cool flame process using an igniter driven by a delay generator. The results show that increasing mixture temperature from room temperature to values below the cool flame region (below 250°C) resulted in an increase in run-up distance. However, as the mixture began to undergo cool flame oxidization, a significant reduction in the run-up distance was obtained (as large as 50%). The sensitization effect was found to occur only at the initial stage of the cool flame oxidation reaction. If the mixture was ignited at times long after the onset of cool flame, the mixture was found to be desensitized and the run-up distance increased. The sensitizing effect of the cool flame partial oxidation may be attributed to the presence of peroxides and free radicals associated with the initial cool flame process. However, these radical species are consumed as the cool flame reaction proceeds and the mixture becomes insensitive again. 

*Keywords:* Sensitization to DDT, Cool flames, Run up distance, Hydrocarbon fuel, Free radicals, Peroxides

## 1. Introduction

This paper is an investigation on the sensitization of a hydrocarbon combustible mixture when it is allowed to undergo the "cool flame" oxidation process [1]. Sensitivity to detonation of an explosive mixture refers to the ease with which detonation can be initiated in that mixture. Although detonation sensitivity is typically quantified by detonation cell size, critical tube diameter, or critical energy necessary to directly initiate detonation, the run-up distance required for deflagration to detonation transition (DDT) can be used as a comparative method to evaluate the relative sensitivity of explosive mixtures with respect to detonation. Thus, while no quantitative link exists between cell size and run-up distance, the measure of run-up distance provides a qualitative and self-consistent measurement of detonation sensitivity.

From chemical kinetics considerations, it is known that the presence of free radicals within a combustible mixture makes it more sensitive to detonation by reducing its induction time [2]. Recently

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Yoshinaka et al. demonstrated experimentally that the presence of free radicals can lead to a reduction of run-up distance in $H_2$-$Cl_2$ detonable mixtures [3]. They irradiated a hydrogen-chlorine mixture contained in a transparent tube with ultraviolet rays, resulting in the photograph-dissociation of chlorine molecules into chlorine atoms (free radicals). This pre-sensitization caused a reduction of the run-up distance to detonation of the mixture when subsequently spark ignited.

The present work investigates the sensitization of a pentane-oxygen mixture by the production of free radicals obtained in the partial oxidation "cool flame" process. Cool flames are combustion waves that occur in gas-phase organic mixtures for temperatures ranging between 200 and 400°C [4]. The cool flame reactions are characterized by a small energy release equivalent to only about 5–10% of the total enthalpy of the reactants, resulting in a temperature increase of the order of 100°C. This heat release is accompanied by weak pressure pulses and the appearance of pale chemiluminescence, and the products of the cool flames are mainly aldehydes, peroxides, and free radicals. While electronically excited formaldehyde seems to be responsible for the chemi-luminescence, the nature of the peroxides is more complicated [5]. In fact, just before the appearance of the cool flame there is an increase of the concentration of organic peroxides that break up, at the onset of the cool flame, into hydrogen peroxides and free radicals [6]. For these reasons, the cool flame oxidation process results in a significant change in the chemical characteristics of the mixture. The cool flame process was originally explained as a chain-branching mechanism suggested by Lewis and von Elbe [7]. However, that mechanism appeared to correspond to a large amount of energy release not verified by experiments. For example, the maximum temperature rise reported in the present study during the cool flame reaction was of the order of 150°C, accounting for only 5–10% of the total enthalpy of the reactants. However, the conclusive demonstration that a chain branching reaction occurs during the onset of cool flame was given by the experimental results of Bonner and Tipper [5] that additionally pointed to the existence of a negative temperature coefficient (NTC) of the reaction as already suggested by earlier experimenters. A proposed NTC mechanism [6,8] shows the following reaction sequence: addition of pentyl radicals to $O_2$ to form pentyl peroxy, pentyl peroxy isomerization, and subsequent reaction with $O_2$ leading to chain branching. This process is typical of the first stage ignition mechanism (cool flame chain branching) and ends when the increased temperature reverses the addition reaction of alkyl radicals to molecular oxygen. This negative temperature coefficient of oxidation essentially shuts off the main chain branching reaction and quenches the ignition. The presence of the above mentioned non-equilibrium species during the cool flame reaction would be expected to sensitize the mixture, leading to a reduction of the run-up distance with respect to the original mixture.

In view of the recent interest in the pulse-detonation engine (PDE), where it is desirable to effect a rapid transition to detonation with insensitive, heavy hydrocarbon fuels, the cool flame sensitization method warrants renewed attention. To date, the effect of cool flame sensitization on DDT was investigated by Shchelkin and Sokolik in the 1930s [9]. Their study reported a significant reduction of the run-up distance in pentane-oxygen mixtures that underwent cool flame oxidation. However, due to difficulties in establishing the exact time of onset of cool flame, it was difficult to find the conditions where the maximum sensitization of the mixture occurred. Also, Shchelkin and Sokolik used the hot detonation tube itself to heat up the mixture, resulting in large temperature gradients inside the tube.

The objective of the present investigation is thus to verify Sokolik's early observation that the cool flame partial oxidation process can lead to a significant reduction of the run-up distance to detonation of heavy hydrocarbon combustible mixtures.

## 2. Experimental procedures

The ideal experiment to investigate the effect of cool flame on the sensitization to DDT of a hydrocarbon-oxygen mixture would be to instantaneously and uniformly heat up the entire mixture and bring it to the cool flame pressure-temperature region. The mixture, contained in a heated detonation tube, would be ignited by a weak spark, and the subsequent deflagration would accelerate up to the point where transition to detonation occurred within the length of the detonation tube. The sensitizing effect would be assessed by measuring this run up distance to DDT, compared to the run up distance obtained in absence of cool flame.

If the mixture is instantaneously and uniformly heated, the reactants would evenly start the cool flame oxidation reaction, and non-equilibrium species such as aldehydes, peroxides, and free radical, would be formed within the mixture as the reaction proceeds [6,10,11]. As a result, time becomes one of the parameters that control the mixture composition during the development of the cool flame process. It is necessary that the concentrations of the chemically active species be essentially "frozen" during the deflagration to detonation transition so that the measured run up distance can be correlated with the

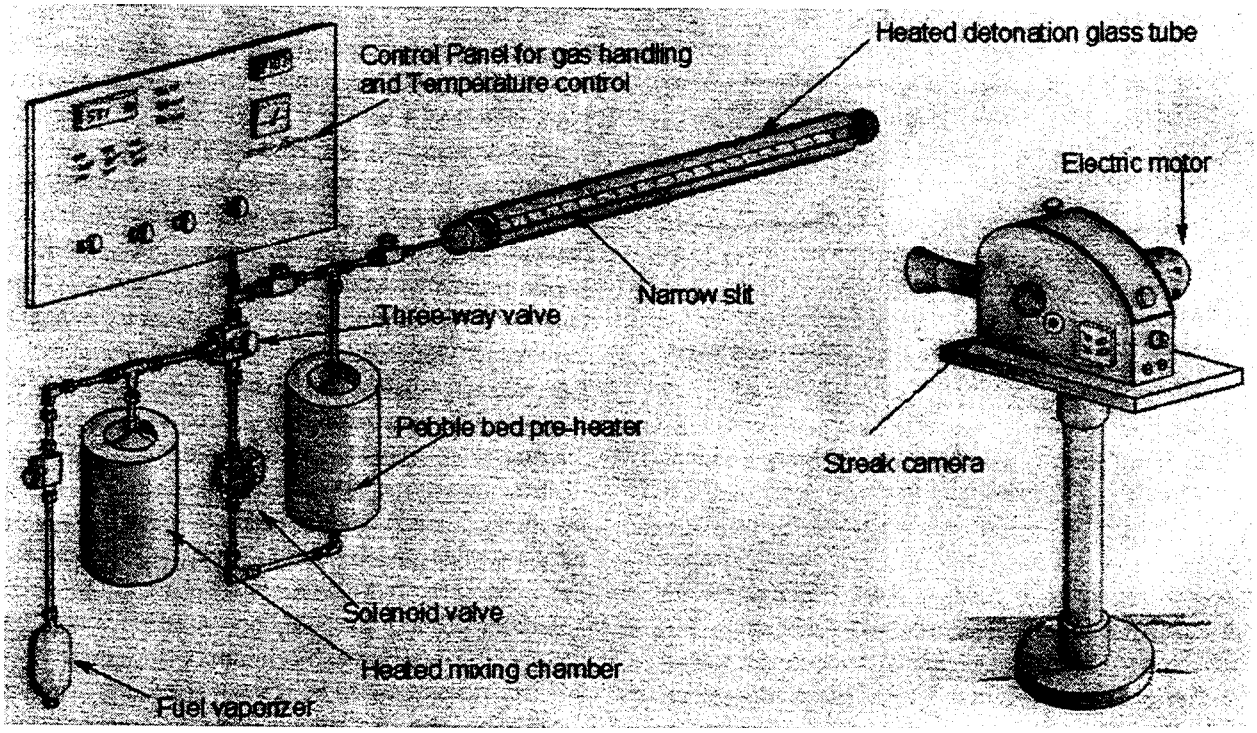


Fig. 1. Experimental set-up.

"instantaneous" mixture composition. Therefore, since the DDT phenomenon takes place within a time scale of the order of a millisecond, the experimental setup (Fig. 1) was designed to ensure the cool flame phenomenon occurred in a time interval of the order of a second.

A fast and uniform pre-heating of the mixture was obtained using a heated pebble bed. The purpose of this pre-heater was to quickly heat up the mixture to a temperature immediately below the cool flame region before filling the heated detonation tube (test section). As a result, only the final temperature increase had to be obtained in the detonation tube, therefore, minimizing the temperature gradient within the mixture and ensuring a homogeneous concentration of non-equilibrium species.

The pebble bed consisted of a 1-liter capacity stainless steel cylindrical vessel filled with 6.3-mm-diameter stainless steel spheres. Heating was provided by two semi-cylindrical ceramic heaters each rated 900 W at 120 V with a surface loading of 13.6 W/cm$^2$. The temperature of the external surface of the pebble bed was monitored by a K-type thermocouple glued on the outer surface of the vessel. The adjustment of the temperature was obtained via a temperature controller (Omega CN2000 Series), which modulated the power output of the heater through a solid-state relay. The cold mixture coming from a mixing chamber passed through this pre-heater before filling a heated detonation tube (test section). The temperature of the pre-heater was chosen after a series of tests to find the maximum temperature (240–260°C) at the working pressure where no cool flame or any other appreciable slow reaction was detected within the mixture. The criterion used to determine that no slow reaction occurred in the mixture was that the run up distance did not change even when the mixture had been kept at these temperatures for several minutes before spark ignition.

The heated detonation tube was a 1.2-m-long heavy wall Pyrex tube with a 2.4 cm internal diameter (Corning Cat. # 237540). Heating was provided by three heating tapes each rated 630 W at 120 V (Omega STH 101-040) longitudinally positioned along the Pyrex tube leaving exposed only a narrow window to allow visual observation of the flame in the tube. To hold the heating tapes in close contact with the tube, they were enclosed in a metal casing that also provided an opening for the photographic recording of the acceleration of the flame. The casing consisted of two semi-circular aluminum cylinders joined along one side by a long hinge so that it could be easily opened to have access to the heating tapes, the tube, and the four thermocouples glued on the surface of the tube to monitor the temperature.

A Shchelkin spiral, consisting of a 0.9-mm diameter steel wire with a pitch of one turn per tube diameter, was used to facilitate acceleration in the initial laminar to turbulent flame transition and to reduce run up distance. These obstacles also had the effect to reduce the shot-to-shot variability of the transition distance to within one tube diameter. Thus,

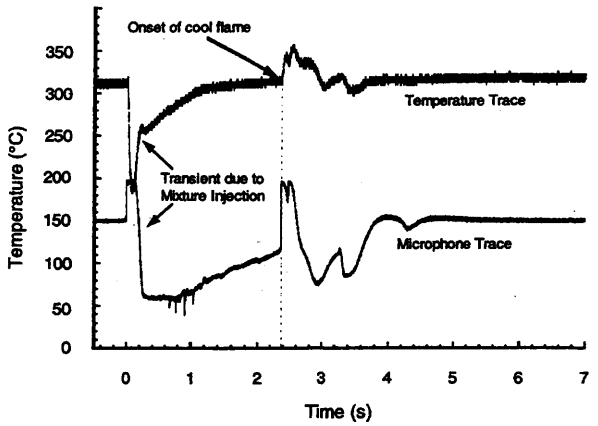


Fig. 2. Temperature and pressure traces indicating onset of cool flame.

the pre-detonation regime in these experiments focused mainly on the fast turbulent deflagration and transition to detonation regime instead of the laminar and weak turbulent flame regime, where pre-sensitization by radicals was expected to play a less important role [12].

A steady, uniform temperature could be maintained along the evacuated tube to within ±5°C, over a range 25–450°C. The onset of cool flame was determined using a 0.001-inch-diameter K-type thermocouple inserted coaxially inside the tube using a hollow ceramic support. In addition, to pick up the weak pressure pulses generated by the onset of the cool flame, an "electret" condenser microphone with built-in FET technology preamplifier (Radio Shack catalog No. 270-092A) was installed at the far end of the tube to check the time response of the thermocouple. The sensitivity of the microphone was 1V/$\mu$bar at 1kHz and the −3dB frequency response extending from 20 Hz to 15 kHz. The microphone was used to indicate the start of the cool flame reaction and not to quantify the amplitude of the pressure waves. Both the thermocouple and the microphone exhibited a transient signal for approximately 400 ms after injection of the mixture into the detonation tube, as seen in Fig. 2. The signals returned to steady state values before the onset of cool flame. The thermocouple and microphone simultaneously reported the same time for the appearance of the cool flame to within a few tens of milliseconds (Fig. 2).

Preliminary experiments conducted in a steel heated tube had shown a large scatter in the time of onset of cool flame. However, the appearance of the cool flame in the glass heated detonation tube turned out to be very reproducible once the temperature of the detonation tube had been set at a constant value. The discrepancy between these observations was attributed to surface chemistry effects of the steel tube on the different species of the heated mixtures. Therefore, the reproducibility of the cool flames in the glass tube was considered as an indication that surface effects were not so significant when a heated glass tube was used.

The mixture was prepared by vaporizing the fuel (n-pentane) into a mixing chamber maintained at a temperature of 50°C. Oxygen was then added and the desired composition was obtained by the method of partial pressures. The mixture composition was kept at an equivalence ratio of $\phi = 1.1$. In the experiment, a solenoid valve was first opened for a controlled time interval to allow the mixture to pass through the heated pebble bed, where the mixture was heated to a temperature immediately below that of cool flame before entering the heated detonation tube. The time necessary to reach the final pressure in the detonation tube was measured to be less than 0.5 s, as monitored by a pressure transducer, whereas the time delay before the onset of the cool flame reaction was of the order of 0.7 s or more. Therefore, a time interval of at least 200 ms existed between when the pressure in the tube reached the final value and the moment when the cool flame started.

The mixture was then ignited by a weak spark obtained from an EG&G TM-11 trigger module capable of discharging about 30 mJ at 30 kV. Each shot was fired at different time delays after injection, permitting observation of the run up distance to DDT at different stages of the cool flame oxidation process.

The acceleration of the flame and its transition to detonation were recorded using the self-luminous streak photography technique. The use of streak photography permitted determining the exact location in the tube where the accelerating flame transited to a detonation. The run-up distance could thus be measured with an accuracy of approximately 0.5 cm. Figure 3 shows a typical self-luminous streak photograph of the DDT process. The onset of detonation is clearly visible and corresponds to a typical "kink" in the combustion front trajectory.

## 3. Experimental Results

Because the cool flame is achieved at high temperatures, the first series of experiments were aimed at separating the effect of higher temperature alone from the chemical effect of the cool flame oxidation. Reference experiments were thus first conducted at temperatures below the cool flame oxidation, to study the effect of temperature alone on the run-up distance. The influence of temperature on the run-up distance of the same pentane-oxygen mixture is shown in Fig. 4. The density of the gas was kept constant at a value of 0.19 ± 0.02 kg/m$^3$ to maintain the same energy content of the mixture at different

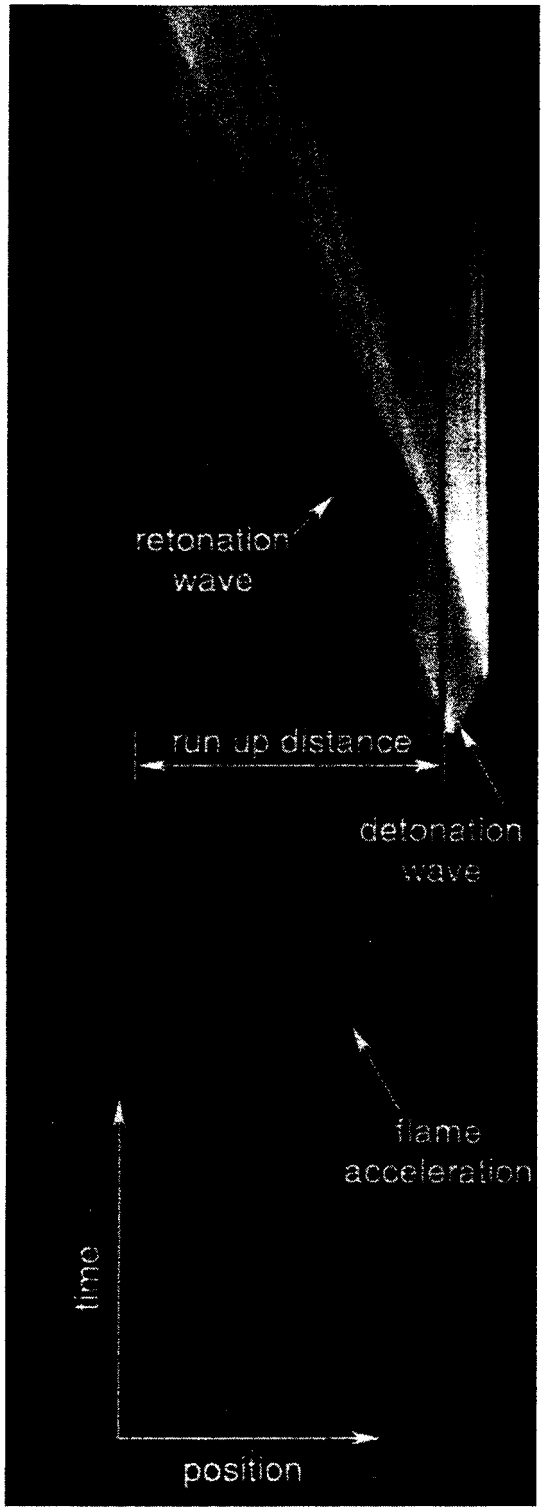


Fig. 3. Sample of streak photograph.

temperatures. Although the density was constant, it can be observed that the run-up distance increased with temperature, a result that can be attributed to the higher sound speed of the mixture, which makes it more difficult to build up sufficiently strong shock waves. The results show that the run-up distance reached asymptotically a value of approximately 40 cm when the temperature of the gas was about

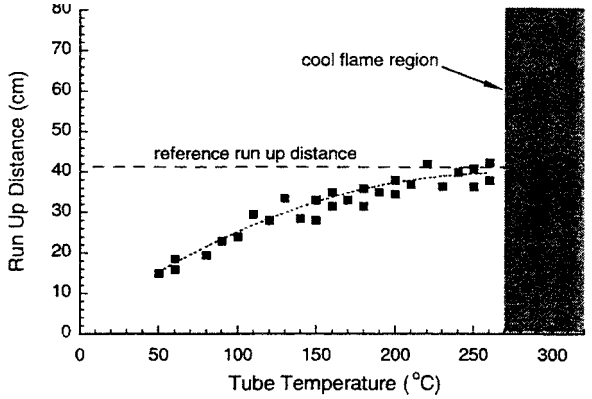


Fig. 4. Run up distance dependency on temperature for pentane oxygen ($\phi$ = 1.1) at a constant density of 0.19 ± 0.02 kg/m$^3$.

250°C. These values of the run-up distance did not depend on how long the mixture was maintained at the corresponding temperature (within several minutes) before spark ignition, since no significant chemical reaction occurred. The limiting value of the run-up distance was then used as the reference run-up distance to compare the effect of the cool flame oxidation process when the mixture was brought into the cool flame temperature region.

The effect of cool flame oxidation on run-up distance is shown in Fig. 5. For this set of experiments, the tube temperature was maintained at a constant temperature of 320°C. At this temperature, the onset of cool flame occurs after 2.4 s from the instant of injection of gas into the detonation tube. The shaded area on the graph indicates the time of the first appearance of the cool flame. When the mixtures were ignited before undergoing cool flame, the measured run-up distance corresponded to the reference value of 40 cm of the heated but unreacted gas. However, as the ignition delay time approached the instant during which the cool flame appeared, a clear reduction in run-up distance was observed, reaching a

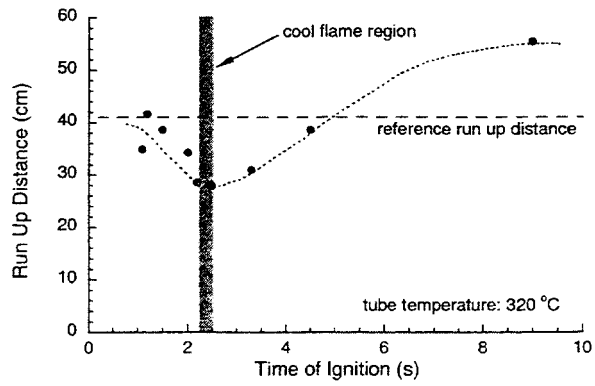


Fig. 5. Effect of cool flame on run up distance in pentane oxygen ($\phi$ = 1.1) at 23 kPa. Tube temperature: 320°C.

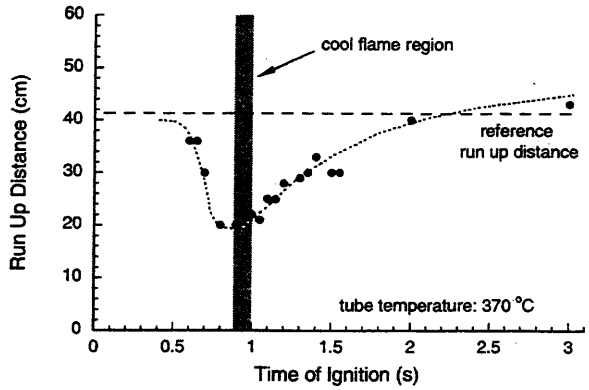


Fig. 6. Effect of cool flame on run up distance in pentane oxygen ($\phi$ = 1.1) at 24 kPa. Tube temperature: 370°C.

minimum value of approximately 30 cm during the cool flame process. When the mixture was ignited after cool flame, the reduction in run-up distance was progressively less pronounced. A de-sensitizing effect was observed when ignition occurred several seconds after the onset of cool flame.

Further results (Figs. 6 and 7) were obtained at higher detonation tube temperatures, for which the onset of cool flame occurred more rapidly, within one second from the instant of injection of the combustible mixture in the heated detonation tube. The general trend was similar to the one observed at a lower temperature (Fig. 5). However, in this case when the mixture was spark ignited during the onset of cool flame, the reduction in run-up distance was more significant, from 40 cm down to 20 cm. A sensitizing effect was visible only if the mixture was ignited within 1000 ms after the first appearance of the cool flame. Further delay in the instant of ignition led to values of the run-up distance comparable with the reference value. If the mixture was ignited long after the cool flame, the run-up distance was longer than the reference value.

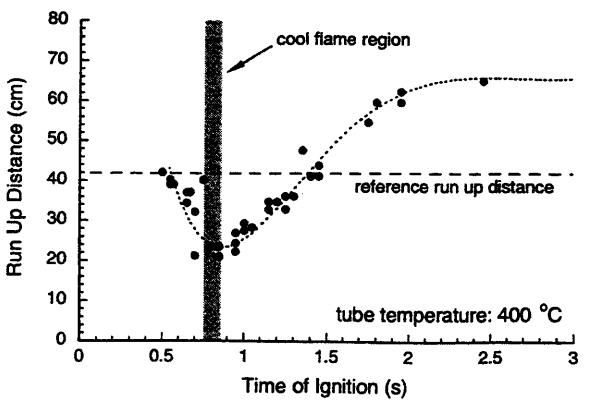


Fig. 7. Effect of cool flame on run up distance in pentane oxygen ($\phi$ = 1.1) at 26 kPa. Tube temperature: 400°C.

## 4. Discussion

The effect of cool flame oxidation on run up distance was explored at three temperatures to verify how the different properties of the cool flame would change the sensitivity of the mixture with respect to DDT. The three temperatures chosen for the investigation were: 320°C, 370°C, and 400°C. The results are summarized in Figs. 5, 6, and 7 that show run up distance to DDT as a function of the ignition timing measured from the instant of filling the tube (opening the solenoid valve). The shadow regions correspond to the intervals within which onset of cool flame was observed, while the dashed lines indicate the reference run up distance as determined in Fig. 4.

The salient result is that all figures show a "V" shaped curve revealing that the run up distance decreases when the mixture is spark ignited simultaneously with the onset of cool flame (within the resolution of the experimental observations and the scattering of the onset of the cool flame reaction). In fact, the run up distance measured when the mixture was ignited before onset of cool flame corresponds to the reference value 40 cm obtained at a temperature of 250°C. However, when the mixture was ignited during the cool flame reaction, the run up distance significantly decreased, especially if the event occurred at high temperatures as demonstrated by Fig. 7. The sensitizing effect of the cool flame reaction does not last longer than 1000 ms, after which the run up distance increases and overshoots the original reference value if the mixture was ignited several seconds after the cool flame.

These results point in the direction that cool flame can have a detonation-sensitizing effect on hydrocarbon-oxygen mixtures to DDT. Even though during the cool flame reaction the mixture loses part of its available chemical energy (~5–10%), the presence of some intermediate products of the partial oxidation seems to promote the transition from deflagration to detonation of the mixture ignited in an obstacle laden tube. The de-sensitizing effect observed when the mixture was spark ignited long after the cool flame reaction can be explained considering the decomposition of the active-species present within the mixture at the beginning of the cool flame, accompanied by the partial loss of total enthalpy of the mixture.

The presence of the Shchelkin spiral had the effect to "bypass" the initial stage of flame acceleration from slow laminar to fast turbulent and the findings of the present study suggest that the presence of chemically active species have a significant effect on the final stage of the DDT process, decreasing the run up distance from 40 cm down to 20 cm, a reduction of 50%.

The chemical sensitization of the cool flame was

particularly evident when the cool flame phenomenon was obtained at the highest temperature (Fig. 7). It was visually observed that at the highest temperatures investigated during the study, the chemi-luminescence of the cool flame reaction occurred quickly and simultaneously along the length of the detonation tube (probably because of the characteristics of the apparatus). This could be an indication of a more uniform oxidization of the combustible mixture that ensured a homogeneous concentration of the intermediate products present in the mixture during the transition to detonation process. In fact, the present setup allowed the time scale of the cool flame oxidation to be increased by lowering the detonation tube temperature permitting the effects of the various stages of the cool flame reaction on DDT to be investigated. The experiments revealed that the slow propagation of the cool flame front along the tube observed at lower temperatures (320°C) did not cause as dramatic a reduction of run up distance as was observed at 400°C. It can be argued that the slow propagation of the cool flame front generated a gradient in concentration of the short-lived intermediate products that did not favor the optimum conditions for the sensitization of the mixture. On the other hand, a more homogeneous concentration of intermediate products was obtained at higher temperatures where a more significant sensitizing effect was observed.

The results can be also explained in view of the NTC mechanism of the cool flame: when the mixture was quickly and uniformly heated to the cool flame region, it was simultaneously conditioned by two opposing reaction mechanisms. On one hand, the rather high temperature promotes the partial oxidation reaction of the fuel that leads to production of active intermediate species, heat release, and chemiluminescence. On the other hand, the temperature increase due to the heat of reaction liberated by the partial oxidation triggers the inhibiting NTC mechanism that tends to slow down the rate of the oxidation reaction to bring the temperature back to the original level. This behavior is described in the temperature trace of Fig. 2 where the temperature of the mixture increased from about 320°C to 370°C during the cool flame reaction and after less than two seconds the temperature decreased to the initial 320°C. Therefore, if the NTC mechanism is sufficiently fast in decelerating the reaction rate, and sufficient heat losses (apparatus dependent) are present to reduce the temperature increase, then the temperature stabilizes to the initial value, the cool flame disappears and the concentration of active species drops to a negligible value. However, if heat losses were not so important, the inhibitor mechanism might not be sufficiently fast to slow down the oxidation reaction rate before the temperature increase starts the thermal acceleration, which would lead to chain-branching and hence auto-ignition of the pre-conditioned partially reacted mixture (two-stage mechanism).

The conditions to obtain the maximum sensitization were found be met when the mixture was quickly and uniformly brought immediately below the NTC temperature region where cool flame is being inhibited, however, with the mixture being so close to the double-stage temperature limit, the smallest disturbance, such that a pressure wave, might be sufficient to bring the mixture in the thermal acceleration state and cause chain branching.

## 5. Conclusion

The results of the present study confirm that when a pentane-oxygen mixture undergoes cool flame partial oxidation, it is more sensitive to detonation as indicated by a reduction of the run-up distance to detonation. The generation of peroxides and radical species at the initial stage of the cool flame oxidation reduces the induction time of the mixture and thus increases the mixture sensitivity to detonation. The production of aldehydes, due to the partial oxidation of the fuel, marks the beginning of the cool flame process that evolves via formation of peroxides and other active species (free radicals) as indicated by the appearance of chemiluminescence (cool flame). The present experimental set-up permitted spreading out this series of events to last several seconds (one to three seconds) during which it was possible to spark ignite the mixture at different stages of the process. The results showed that, during the cool flame process, the mixture underwent significant transformations of its chemical kinetic characteristics, as indicated by a substantial decrease of the run-up distance to detonation by a factor of two when the mixture was spark ignited promptly after the appearance of the cool flame. The chemical composition continued to evolve after the end of the chemiluminescence. In fact, when the mixture was spark ignited several seconds after the appearance of the cool flame, the run-up distance increased to values greater than those observed before the cool flame, indicating a de-sensitizing effect with respect to detonation. These observations point out that the chemical species responsible for the sensitization effect are present only at the very early stage of the cool flame process.

## Acknowledgments

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## Appendix 6: Sensitization of Hydrocarbon-Oxygen Mixtures to Detonation via Cool Flame Oxidation

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# SENSITIZATION OF HYDROCARBON-OXYGEN MIXTURES TO DETONATION VIA COOL-FLAME OXIDATION

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The effect of cool-flame partial oxidation on the detonation sensitivity of hydrocarbons was experimentally investigated. Sensitivity to detonation was quantified by measuring the detonation cell size using the smoked-foil technique. A rich pentane/oxygen mixture was preheated in a pebble bed before filling a heated glass detonation tube to subatmospheric pressure. Cool-flame reaction, monitored by a thin K-type thermocouple, occurred in the detonation tube after a known time interval. The mixture was ignited by a weak spark and onset of detonation was monitored using a streak camera. A smoked foil was inserted in the far end of the tube to permit the measurement of the cell size of a well-developed detonation. The results show that the cell pattern becomes regular at high temperature, but the average cell size practically does not change. However, when the mixture was detonated while undergoing the cool-flame reaction, a significant reduction of the cell size was obtained. The sensitizing effect was found to occur in the initial stage of the cool-flame reaction.The explanation of the sensitizing effect of the cool-flame reaction was investigated by using a chemical kinetic model to simulate the cool-flame reaction and identify the chemical species that may be responsible for the observed results. By taking snapshots of these chemical concentrations during the simulated cool flame, these species were used as reactants in a time-dependent, spatially homogeneous calculation to compute the induction kinetics for a Chapman–Jouguet detonation. The numerically computed induction times follow the experimentally observed cell sizes and confirm that the sensitizing effect of the cool-flame reaction may be attributed to the presence of free radicals associated with the beginning of the cool-flame process. However, these radicals are consumed as the cool-flame reaction proceeds and the mixture becomes insensitive again.

## Introduction

From a chemical kinetic point of view, it is known that free radicals enhance the detonation sensitivity of combustible mixtures by reducing the induction time. In a series of pioneering experiments, Shchelkin and Sokolik [1] reported a reduction of the run-up distance to detonation (DDT) of a pentane/oxygen mixture when it was spark ignited in the "cool-flame region." Cool flames are combustion waves that occur in gas-phase organic mixtures in the temperature range between 450 and 650 K. The cool-flame reactions are characterized by a partial combustion of the reactants where only a small fraction of the total chemical energy is released [2]. The phenomenon [3] is accompanied by a pale chemiluminescence and the production of aldehydes, peroxides, and free radicals. Shchelkin and Sokolik's conclusion was that relatively long-lived peroxides and free radicals were responsible for the increased sensitivity. Recently, Romano et al. [4] have confirmed Sokolik's early results and demonstrated that a reduction of about 50% in the run-up distance can be obtained when a pentane/oxygen mixture is spark ignited while it uniformly undergoes the cool-flame partial oxidation process. However, care must be taken in using the run-up distance to detonation as a measure of the detonation sensitivity of a combustible mixture since it can at best provide only a qualitative measure of the detonation sensitivity. The run-up distance to DDT is not independent of the fluid dynamics involved during the acceleration of the flame, and involves the transition between different mechanisms of combustion wave propagation, which may not depend on the induction kinetics of the mixture. Detonation sensitivity is best measured experimentally by parameters such as the detonation cell size [5]. Therefore, the objective of the present study is to experimentally measure the detonation sensitivity of an *n*-pentane/oxygen mixture while it is undergoing the cool-flame oxidation process by measuring the detonation cell size. A complimentary theoretical study based on a model of pentane combustion [6] is also used to numerically simulate the experimental results of the investigation to provide

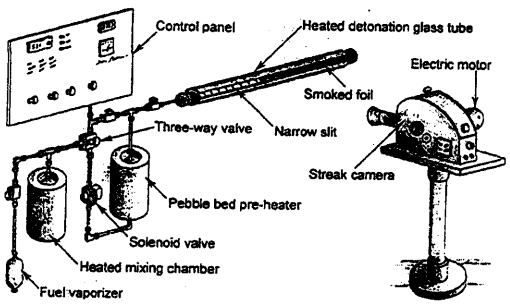


FIG. 1. Experimental setup.

a better understanding of the exact mechanism responsible for the sensitization.

## Experimental Apparatus and Procedure

The experimental apparatus is illustrated in Fig. 1, which was described in detail in a previous work [4]. To achieve a well-controlled and reproducible experiment, a pebble-bed preheater was used to uniformly heat up the mixture to a temperature below the cool-flame region. The uniformly preheated mixture was then injected in an evacuated heated detonation tube, where it underwent the cool-flame process. The detonation tube was a 1.2-m-long, 2.4-cm-internal diameter glass tube provided with a 0.5-m-long Shchelkin spiral made from a 0.9-mm-diameter steel wire wound with a pitch of one tube diameter. Heating of the tube was achieved by three separately driven heating tapes placed lengthwise along the tube, leaving a 10-mm-wide open slit to allow visual observation of the events inside the tube. Ignition of the mixture was achieved using a spark generator EG-G TM11 module. The tube and the heating tapes were enclosed in an insulated metal casing provided with a slit to allow photographic recording of the transition to detonation. Onset of cool flame was indicated by the temperature trace of a K-type thermocouple (0.050 mm thick) inserted coaxially inside the tube.

All experiments were conducted at constant mixture composition ($\phi$ = 1.1) and density ($\rho$ = 0.170 kg/m$^3$ ± 5%), while varying the instant of ignition by using a delay generator. In this manner, the mixture was spark ignited at different times with respect to the instant of the onset of the cool flame. Initiation of detonation was observed with the use of a streak camera, and the detonation sensitivity was measured using the smoked-foil technique. The smoked foils were 0.127 mm thick, 50 mm wide, and 300 mm long and located at the opposite end of the tube from the igniter. They were rolled lengthwise and carefully inserted in the detonation tube. The temperature range chosen for this study was 640–655 K, where the expected delay time for the onset of cool flame was slightly less than 1 s after the injection of the mixture into the heated detonation tube from the preheater [4].

## Experimental Results

Experiments were first carried out to determine the effect of temperature alone on the detonation cell size without cool-flame reaction. The detonation cell pattern (for *n*-pentane/oxygen mixture at equivalence ratio $\phi$ = 1.1 and pressure of 25 kPa) at about 630 K was found to be very regular with an average cell size of 5–6 mm, while the detonation cell pattern at room temperature for the same density of the mixture was found to be irregular but with nearly identical average cell size (Fig. 2). The detonation cell-size measurements provide clear evidence that the effect of temperature, in the range 300–600 K, does not decreases the cell size and it does not alter the detonation sensitivity of the mixture, provided the density of the mixture remains constant [7,8].

Onset of cool flame was indicated by a sudden increase of the temperature of the mixture as indicated by the thermocouple located inside the tube. A typical temperature trace is shown in Fig. 3 that indicates the onset of two cool flames at approximately 0.5 and 0.9 s after injection of the mixture into the tube.

When the mixture was detonated at the beginning of the cool-flame oxidation, a significant reduction of the detonation cell size was observed. The average dimension was found to be 2–3 mm, compared with 5–6 mm obtained by detonating the mixture before the start of the cool flame. If the mixture was ignited after a long delay time, however, when the cool-flame reaction had completed, the cell size returned to the original value or sometimes was even larger (Fig. 2). This increase in cell size after a long delay indicates a desensitizing effect in the mixture. The results are summarized in Fig. 4, which shows the variation of cell size as a function of the time delay between mixture injection and ignition. The shaded area indicates the time interval during which the cool-flame reaction occurred.

## Numerical Simulation

The reaction mechanism used for this study has successfully been applied previously by Ribaucour et al. [9,10] for modeling experimental data on autoignition of the three isomers of pentane in a rapid-compression machine. In the present numerical study, a constant-volume, static reactor was considered with *n*-pentane as the fuel at an equivalence ratio of $\phi$ = 1.1, an initial temperature of 593 K, and an initial pressure of 25 kPa. A heat-transfer model was used, assuming a reactor wall temperature of 593 K and a characteristic heat transfer time

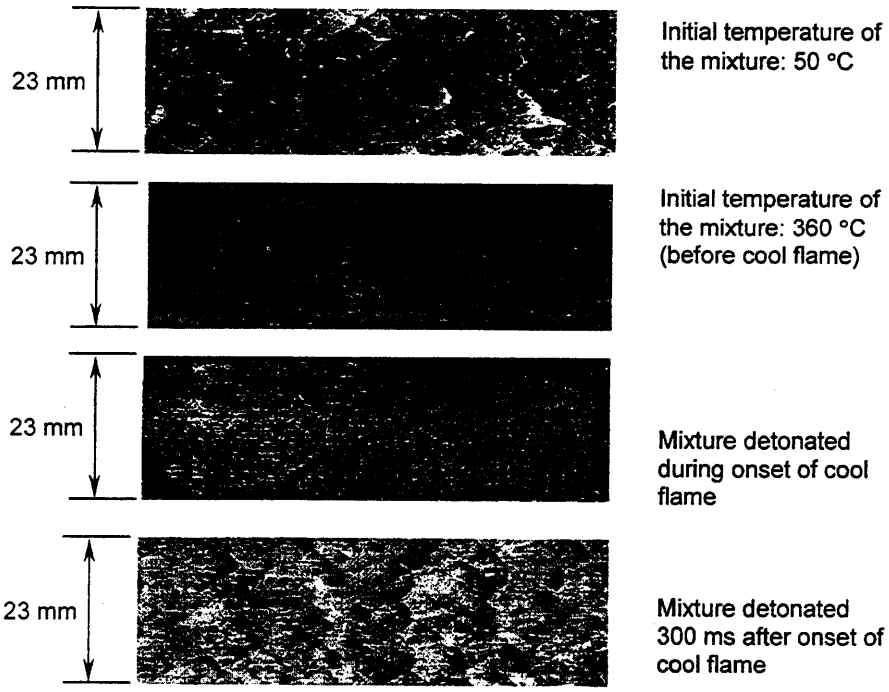


FIG. 2. Samples of smoked foils.

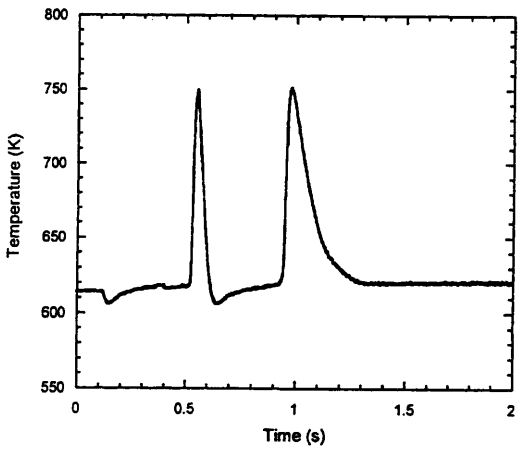


FIG. 3. Temperature trace of 0.050 mm thick K-type thermocouple indicating the onset of two cool flames.

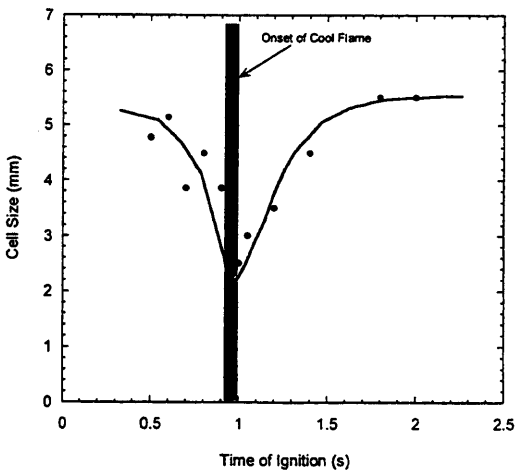


FIG. 4. Effect of cool flame on detonation cell size in $n$-pentane/oxygen ($\phi = 1.1$) at constant density ($\rho = 0.170$ kg/m$^3$ ± 5%).

of 0.1 s. Calculations were also performed with other heat-transfer times. With longer heat-transfer times, the cool flames occurred earlier. With shorter heat-transfer times, the cool flames occurred later or were entirely suppressed. So, the heat-transfer model was adjusted to match the experimentally obtained thermocouple traces. The overall heat-loss rate from the reactive mixture to the detonation wall tube was described by the expression $Q = hA(T - T_{wall})$, where $Q$ is the heat-loss rate, $h$ is the convective heat-transfer coefficient, and $A$ is the inner area of the detonation tube. $T$ and $T_{wall}$ are the temperature of the gas inside the tube and the wall, respectively. A value of $h = 310\text{W}/(\text{K} \cdot \text{m}^{-2})$ was chosen to give about the same characteristic time for the cool-flame event as observed in the experiments.

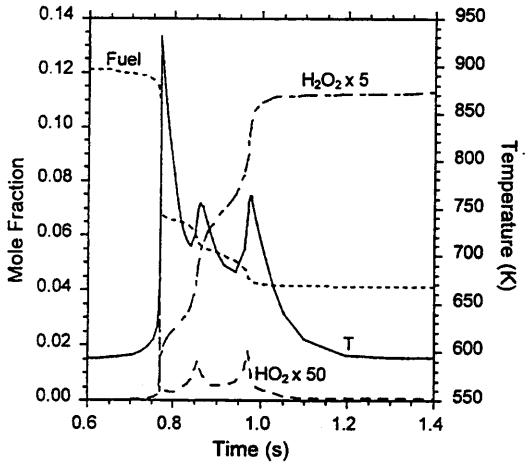


FIG. 5. Simulated temperature history of cool-flame reaction and chemical-concentration profiles.

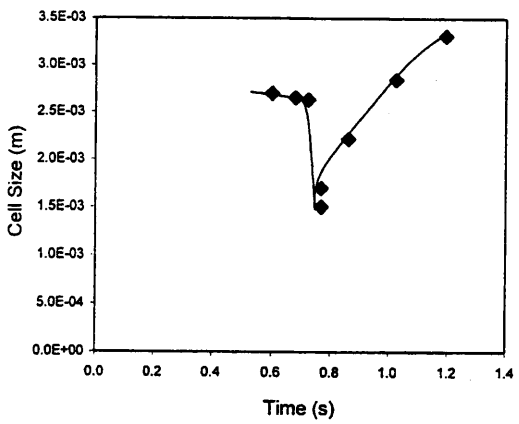


FIG. 6. Simulation of effect of cool flame on detonation cell size in *n*-pentane/oxygen.

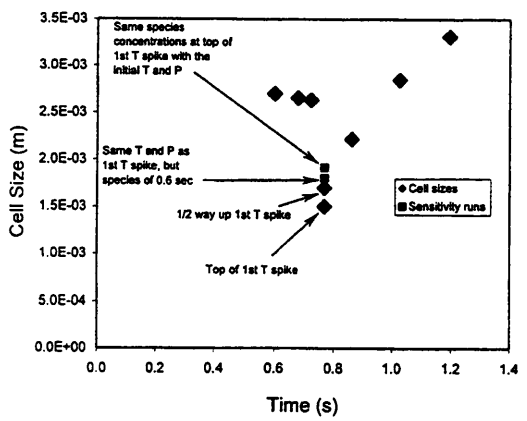


FIG. 7. Sensitivity analysis calculations.

Under these conditions, three distinct cool flames were observed in the computed results, until fuel consumption precluded further cool-flame activity. Multiple cool flames are common in fuel/oxygen mixtures under similar conditions [11]. The results of the cool-flame simulation are summarized in Fig. 5, showing the temperature and concentrations of *n*-pentane, $HO_2$, and $H_2O_2$. The overall duration of the cool flame was approximately 0.5 s, and each of the three cool flames is noted by a step decrease in pentane, a step increase in $H_2O_2$, and spikes in temperature and $HO_2$ concentration. Other radical species such as OH and many of the alkylperoxy radicals had concentration profiles similar to that shown for $HO_2$ in Fig. 5. The overall fuel consumption in the cool-flame period is approximately 67%, from 0.12 to 0.04 mole fraction. The fuel decrease, the $HO_2$ levels, and the temperature spikes all indicate that the first cool flame was somewhat more vigorous than the second or third. None of the cool flames reached the temperature at which the $H_2O_2$ decomposes, so a true ignition event was not observed [6].

Beginning with the completely unreacted mixture at 0.6 s in Fig. 5 until the conditions following the end of the cool flame at 1.2 s, a series of "snapshots" were taken of the chemical compositions at different instants during the cool-flame simulation in Fig. 5. For each instant, postshock induction time calculations were executed using the Chapman–Jouguet (CJ) conditions to define the shock speed, assuming that the reactive system is "frozen" during the passage of the shock wave. From the computed induction times, cell sizes were calculated at each point, assuming that the cell size was 50 times the induction length, similar to results observed for fuel/oxygen mixtures in previous kinetic modeling studies [12].

The results of the simulation were remarkably similar to the experimental data as shown in Fig. 6. The time of the first cool-flame temperature peak ($T > 900$ K) is at 0.769 s. At 0.6 s, the cell size is 2.7 mm and remains constant until dropping at 0.768 s to 1.7 mm and falling to a minimum of 1.5 mm at 0.769 s when the cool-flame temperature reaches its highest value. Only 300 ms after the beginning of the simulated cool flame, the calculated cell size is 3.3 mm, reflecting the same desensitizing effect observed during the experiments.

A series of sensitivity analysis calculations was performed to try to isolate the features of the cool flame responsible for the computed reductions in cell size. One at a time, specific species concentrations during the cool flame were varied to see if any of them could produce the type of variations in computed cell sizes seen here. However, these sensitivity studies indicated that no single species from the cool flame could be found responsible for the observations, and while the three temperature peaks during the cool flame produced somewhat reduced cell sizes, the

cell-size total reductions could not be attributed only to these temperatures. As shown in (Fig. 7), if the mixture composition immediately prior to the cool-flame reaction ($t$ = 0.6 s) is brought to the same temperature and pressure that exist at the cool-flame peak, a significant reduction in cell size occurs. Likewise, if the composition at the cool-flame peak ($t$ = 0.769 s) is frozen and brought to the same temperature and pressure as the initial mixture prior to reaction, the increase in mixture sensitivity is nearly the same. Thus, while both radical concentration and temperature have an influence on the detonation sensitivity, their combined effect is responsible for the observed decrease in induction time. The only way to produce the computed cell-size results was to combine the effects of enhanced radical concentrations and higher temperatures, as indicated in Fig. 7.

## Discussion and Conclusion

Experiments were carried out to examine the effect of "cool-flame" preoxidation of a hydrocarbon/oxygen mixture on the detonation sensitivity of a pentane/oxygen mixture. During the experiment, the mixtures were first heated up rapidly to initiate a cool flame, then, at different stages during this process, the mixtures were detonated, and the detonation cell size was measured using the smoked-foil technique.

The kinetic model used in this work captured the most important features of the phenomena encountered. The simulated temperature profiles of the cool flames were very similar to the experimental traces obtained with the use of thermocouples [4], although the computed temperature peaks were 200 K higher than the experimentally measured cool flames. This was due to the limited spatial resolution and thermal inertia of the thermocouple. The kinetic model showed the following reaction sequence: addition of pentyl radicals to $O_2$ to form pentyl peroxy, pentyl peroxy isomerization, and subsequent reaction with $O_2$ leading to chain branching. This process is typical of the first-stage ignition mechanism (cool-flame chain branching) and ends when the increased temperature reverses the addition reaction of alkyl radicals to molecular oxygen. This negative temperature coefficient of oxidation shuts off the main chain-branching reaction pathway and halts the ignition. Computed induction times and cell sizes qualitatively reproduced the experimental observations without extrapolating from any data point, but a linear correlation was used to calculate the characteristic cell size from the induction length. The constant is generally chosen between 30 and 50, where 30 usually matches the cell size of light hydrocarbons. The assumption of a cell size of 50 times the induction length does not interfere with the generality of the results of the investigation.

In relating the computed kinetic results to the experimental observations, it is essential to remember that the computations describe a single, idealized spatial point, and there is no consideration of variations in composition or temperature in the reactive medium. Even if the assumption is accurate that spatial species transport is unimportant, heat transfer to the walls of the detonation tube produces a non-uniform temperature field that will affect the observations. These non-uniformities will, in effect, smear out the results of Fig. 6 over the reactive mixture in the tube, so that, although at each location the mixture may be passing through the cool flame of Fig. 5, not all of the reactive mixture locations will be exactly in phase with each other. This helps explain why the three cool flames were not observed in the experiments, since they are occurring and not occurring throughout the combustion chamber over a period of time. The same argument shows that the most sensitive mixture conditions in the first cool flame will also be occurring at a range of times in the reactive mixture, so that sensitization will persist for a longer time than that computed by the idealized kinetic model.

As noted above, the modeling analysis did not indicate that any specific species in the cool flame is alone responsible for the observed sensitization. Instead, the combination of elevated temperature and radical levels in each cool flame provides the shorter induction time and smaller cell size. Although the kinetic modeling indicates these peaks occur at only a few locations in the cool-flame region, spatial non-uniformities in the experiments can distribute these cool-flame reactive peaks within the reactive mixture over a time interval that is somewhat longer than in the idealized computed results would indicate, effectively diffusing the sharp cool-flame peaks into a broad range that is still sensitized overall.

The kinetic model also shows why the effect of the cool flame first sensitizes the reactive mixture and then in effect desensitizes it. The considerable amount of fuel consumption that occurs from the series of cool flames means that the post-cool-flame mixture has much less exothermicity associated with it than the initially unreacted mixture, and the resulting larger cell sizes are the product of the different CJ conditions in the partially reacted gases.

While the numerical simulation was able to explain the kinetic mechanism of the cool-flame reaction indicating the global effect of temperature and active free radical concentrations, the experimental results conclusively demonstrate that the cool-flame phenomenon can lead to a significant increase of the detonation sensitivity of heavy hydrocarbon mixtures.

*Acknowledgments*

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## Appendix 7: Effect of Transient Gas Dynamic Processes on the Impulse of Pulse Detonation Engines

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# Effect of Transient Gasdynamic Processes on the Impulse of Pulse Detonation Engines

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## Introduction

In a pulse detonation engine (PDE), thrust results from the expansion of the high-pressure and temperature products of a detonation. Much of the effort in PDE development has been focused on the rapid initiation of detonation to achieve detonation in a distance compatible with the dimensions of an engine. The question of whether the impulse generated depends on different gasdynamic processes, such as direct initiation, deflagration to detonation transition (DDT), or constant volume explosion, becomes a valid one.

In the present study, the impulse produced by a single-cycle hydrogen–oxygen PDE is experimentally investigated. The goal is to determine the effect of transient gasdynamic processes on impulse. The impulse produced by direct initiation is compared to that produced by DDT for two different initiation locations, at the thrust wall and at the open end. The equivalence ratio is varied to control the run-up distance (RUD). The impulse is measured in two ways: the ballistic pendulum method and the integration of the end wall (thrust wall) pressure. The former, the ballistic pendulum method, was first applied to measuring the impulse generated by a detonation by Nicholls et al.[1] and has recently been used by Cooper et al.[2] and Daniau et al.[3] to measure the effect of obstacles and nozzles on the impulse generated by a single detonation pulse. Harris et al.[4] also used a ballistic pendulum to study the effect of nitrogen dilution and compared the impulse for the cases of direct initiation and DDT initiated from the closed end of the tube. In the ballistic pendulum technique, the amplitude of swing of a pendulum-mounted PDE provides a direct measurement of the total integrated thrust. The latter technique, integrating the end wall pressure, is more typically used in PDE experiments, but will only produce an accurate measurement of impulse if friction and other momentum losses are negligible.

## Experimental Setup and Procedure

The experimental setup, as shown in Fig. 1, consisted of a smooth-wall stainless steel detonation tube 2.10 m long with a 6.35-cm inner diameter and closed at one end. The tube had a mass of 40 kg. It was equipped with 10 ports along its length to accommodate pressure transducers and ionization probes. Two pressure transducers measured both the end wall and open end pressure histories. The ionization probes recorded the time of arrival of the combustion front. The DDT process was initiated via a 30-mJ automotive-type spark plug, and the direct initiation was achieved via an exploding wire delivering up to 800 J. The igniter could be moved from the thrust wall to a port located 14.5 cm from the open end. The detonation tube was suspended by metal wires from supports located 2.635 m above the tube, and it was free to swing. A video camera captured the motion of the pendulum, from which the total specific impulse $I_{sp}$ could be determined as follows:

$$I_{sp} = M_t/(g \cdot M_m) \cdot \left\{2g\left[L_w - \left(L_w^2 - X^2\right)^{\frac{1}{2}}\right]\right\}^{\frac{1}{2}} \quad (1)$$

In Eq. (1), $M_m$ is the initial mass of the mixture, $M_t$ is the mass of the tube, $L_w$ is the height of the supporting wires, $g$ is the gravitational acceleration, and $X$ is the horizontal displacement of the tube. The open end was sealed with a 0.0254-mm Mylar® diaphragm before each experiment. Control experiments were done with diaphragm thicknesses ranging from 0.023 to 0.254 mm, and no variation in impulse larger than the experimental scatter inherent to the experiment was observed. The tube was evacuated and filled with a hydrogen–oxygen mixture at ambient temperature and pressure by means of calibrated choked orifices. The tube was filled to 1 atm and then continuously flushed with 10 tube volumes of gas to ensure a uniform mixture. Before initiation, the hoses of the gas-handling system were disconnected from the tube to prevent interference with its motion.

## Results and Analysis

By varying the equivalence ratio, the RUD could be varied. This distance (as measured from the ignition point) required for the flame to accelerate to a Chapman–Jouget (CJ) detonation, when initiated via a weak spark, is plotted in Fig. 2. A transition to detonation via DDT was only observed in this tube for equivalence ratios between $\Phi = 0.2$ and 1.8. The RUD did not vary when the location of the initiation was moved from the closed to the open end. In the case of the direct initiation via an exploding wire, the first velocity measurement in the tube was always the CJ velocity, and the detonation was assumed to form instantaneously. The propagation of the detonation and the blowdown process took place over a short period

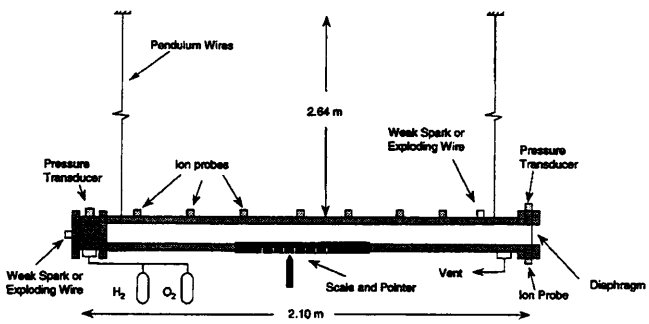


**Fig. 1 Experimental setup showing igniter location for initiation at both the closed and open end.**

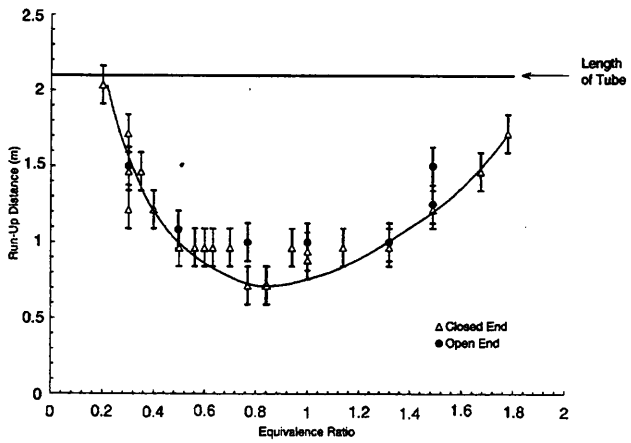


**Fig. 2 RUD to detonation as measured from the point of initiation as a function of fuel equivalence ratio for the weak spark initiation from the closed and open end.**

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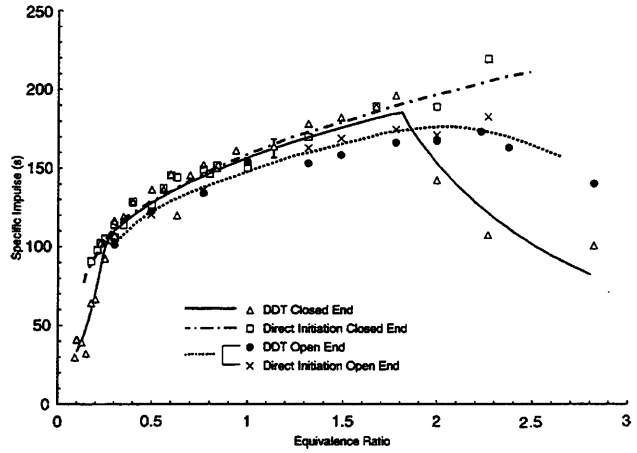
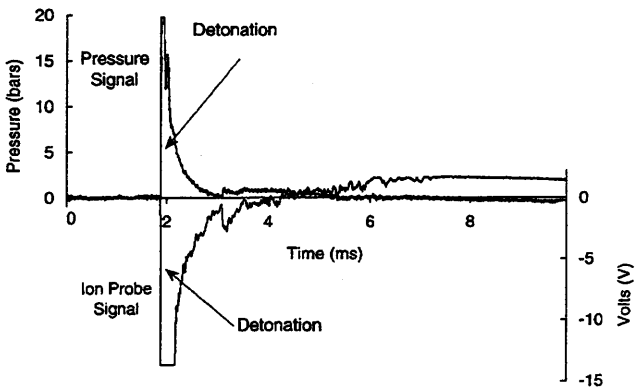
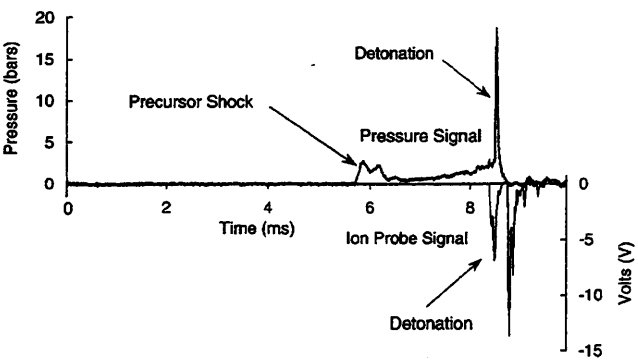



**Fig. 3 Specific impulse as a function of fuel equivalence ratio for different initiation methods.**




**a) Early DDT, Φ = 1.00**




**b) Late DDT, Φ = 0.17**

**Fig. 4 Pressure transducer (positive signal) and ion probe (negative signal) records at the open end of the tube for the cases of a) early DDT and b) late DDT ignited at the closed end; note the presence of nonreacting precursor shock in case of late DDT.**

of time (10–20 ms) when compared to the rise time of the tube (900–1000 ms). The momentum transfer to the tube was, thus, considered instantaneous for the four different gasdynamic processes studied.

Both impulse measurement techniques (ballistic pendulum and end wall pressure integration) exhibited good reproducibility, but the impulse from the pressure integration was consistently larger by 15–30%. Because the ballistic pendulum method takes into account all forces acting on the tube, the results obtained via this technique will be reported in this publication.

In Fig. 3, the $I_{sp}$, as measured by the ballistic pendulum technique, is plotted as a function of equivalence ratio. One typical error bar is presented ($\Phi = 1.2$) and is representative of the average experimental reproducibility. This is obtained from three to five experiments at the same conditions. For a fixed equivalence ratio, the energy content of the mixture is the same, and the comparison of the different initiation cases can be performed. Direct initiation and DDT at the closed end both produced the same impulse for equivalence ratios between $\Phi = 0.3$ and 1.8. For equivalence ratios below $\Phi = 0.3$ or above $\Phi = 1.8$, direct initiation at the closed end consistently produced more impulse than DDT. In this range ($\Phi < 0.3$ or $\Phi > 1.8$), DDT either occurred in the last quarter of the tube or did not occur in the tube at all. The presence of a precursor pressure wave ahead of the combustion front was verified by examining signals from the pressure transducer and ion probe located 1.5 cm from the open end of the tube as shown in Fig. 4. In the case of an early DDT (Fig. 4a) at an equivalence ratio of $\Phi = 1.00$, the first wave to encounter the diaphragm was a detonation wave, with the combustion front closely coupled to the leading shock. In Fig. 4b, the pressure signal for a late DDT at an equivalence ratio $\Phi = 0.17$ shows a precursor shock arriving 2.5 ms ahead of the main combustion front. This precursor compression wave, permitted by a late or absent DDT, ruptured the diaphragm before the arrival of the combustion front and resulted in the venting of unburned mass and a lower $I_{sp}$.

When the mixture was initiated from the open end, no significant difference between DDT and direct initiation was observed over the entire range of fuel equivalence ratio, as shown in Fig. 3. We note that the specific impulse from the initiation at the open end is consistently 15% lower than that of the initiation from the closed end (cf. Ref. 5). This difference is, however, of the order of the experimental scatter.

## Conclusions

The impulse of a single-cycle PDE for different gasdynamic processes has been investigated. These different processes were obtained by varying the initiation method and location. The results show that when initiating from the closed end of the tube, the impulse produced by direct initiation and DDT is the same, as long as all of the mixture is burned inside the tube. This result agrees with the experiments of Harris et al.[4] using propane–oxygen mixtures. Initiation from the open end also exhibited an independence of the initiation technique (direct initiation vs DDT). The impulse generated by initiation from the open end is similar to the case of initiation from the closed end, as previously noted in the study by Zitoun et al.[5] that used integrated end-wall pressure to show the independence of the impulse on the point of initiation. In the present study, when initiating from the open end, the impulse appears to be slightly, but consistently, lower than that for the case of initiation at the closed end. These results strongly suggest that, to a first-order approximation, the impulse generated by a single cycle PDE is only a function of the chemical energy content of the combustible mixture and is independent of the details of the energy release mechanism.

## Acknowledgments

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# Supersonic Wave/Blade-Row Interactions Establish Boundary Conditions for Unsteady Inlet Flows

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THE computation of unsteady flows in high-speed airbreathing inlets requires a compressor-face boundary condition (CFBC). The physical basis for the analytical or numerical formulation of a realistic CFBC is the acoustic reflection coefficient of the operating compressor. In Ref. 1 an approximate, one-dimensional method is offered to calculate this information for a single blade-row compressor, when the total approach velocity (vector sum of axial and tangential components, relative to the rotor blades) is subsonic. The present Note extends the calculation to the practically important case where the total approach velocity is supersonic and the axial component is subsonic. (In this Note, the term "supersonic" refers to this limited range.) The background, motivation, physical model, method of analysis, and nomenclature described in Ref. 1 apply to this Note without change and are not repeated here. Familiarity with Ref. 1 is essential to the understanding of this Note.

In supersonic cascade flows expansion and compression waves can propagate upstream and can modify the approach flow, which makes them considerably different from subsonic cases. It has been well established[2,3] that a steady, uniform, supersonic flow upstream of an infinite, linear cascade of blades can exist only for a unique incidence angle. The existence of such an incidence implies that an upstream moving acoustic disturbance (which might be initiated by a downstream-moving disturbance arriving to the blade row) cancels the initial disturbance, restoring the undisturbed upstream flow. The unique incidence angle can be determined in the knowledge of the blade geometry and the upstream Mach number (methods given in Ref. 2). The unique incidence angle is generally small, several degrees only.

In the following, the exit Mach number is assumed to be subsonic, which is a practically common situation. This assumption also defines a unique steady flow when using the simple mean flow method of Ref. 1. The choice of subsonic outflow implies the presence of shocks (and, hence, a total pressure loss) in the blade passage. The effect of total pressure losses on the reflection coefficient is demonstrably small and a reasonable estimate is sufficient. Shock loss may be estimated as that associated with a normal shock at the upstream Mach number $M_u$. The estimation of viscous losses may be made on the basis of empirical information valid for similar blade geometries.

The analysis deals with a transient initiated by the arrival of an acoustic step change to the blade row, the goal being the prediction of the magnitude of the reflected wave, which is also a step change. The equations used in the present analysis are the same as those of Ref. 1, with one exception. In the subsonic case, it was assumed that the direction of the exit flow, after completion of the transient, is the same as the direction of the undisturbed exit flow [Eq. (25) in Ref. 1]. In the supersonic case, this requirement is dropped, and the unique incidence requirement is imposed on the entering flow. It is assumed that the response of the blade row has to be such as to restore the incidence angle (in region 3) to its original, unique value (in region 1). This assumption implies that

$$w'_{3y} = w'_{3x} \tan \beta_u \tag{1}$$

Because neither the incident nor the reflected acoustic wave can change the tangential velocity, the tangential velocity disturbances are zero in all upstream regions (1, 2 and 3). Equation (1) then forces the axial disturbance in region 3 to be zero also, which means that the region 3 velocity vector is identical to the undisturbed, region 1 velocity vector. The conclusion is that the imposition of Eq. (1) is equivalent to the assumption of constant (upstream) velocity. This is one of the traditional assumptions that has been applied in the past, without justification, to flows with any approach Mach number. The analysis of Ref. 1 showed that this assumption does not apply for a subsonic approach flow. The present analysis shows that the constant velocity condition is in fact applicable in the supersonic range.

The calculations are simple and are omitted. The acoustic wave coefficients are as follows:

$$A_- \equiv \frac{p'_3 - p'_2}{p'_2} = 1 \tag{2}$$

$$A_+ \equiv \frac{p'_4}{p'_2} = \frac{2M_{ux}\sqrt{\chi}}{\sigma(1 + M_{dx})} \tag{3}$$

The analysis also predicts a downstream-convecting vorticity wave. The corresponding vorticity induction coefficient is given by

$$V \equiv \frac{\rho_u a_u w'_{4y}}{p'_2} = 2\frac{1 - \sqrt{\chi}M_{ux}/\lambda\sigma}{\sqrt{\chi}M_{dx} \tan \beta_d} \tag{4}$$

Equation (2) states that for supersonic flow the reflection coefficient is constant with a value of unity. This result is in excellent agreement with two-dimensional, inviscid Euler solutions obtained by Paynter to the same problem.[4] His solutions clearly indicate that for supersonic approach flows the reflection is such that the velocity direction in region 3 is the same as in region 1, in agreement with Eq. (1). Because $A_-$ is independent of the mean flow properties, the mean flow parameters need not be known to compute this coefficient. In contrast, the calculation of the acoustic transmission and the vorticity induction coefficients does require the knowledge of all steady flow parameters, such as inlet Mach number, inlet/exit flow angles, passage height change, and loss coefficient.

The wave/blade interaction problems for stationary and moving blade rows are identical provided they are stated in coordinates fixed to the blades. If the inflow parameters are given in the stationary frame, then the solution process for a moving blade row consists of transforming all mean flow quantities to the blade-fixed coordinate system and subsequently calculating the wave coefficients using Eqs. (2–4).

For the special case of unloaded flat plates with no area change ($\beta_u = \beta_d = \beta$, $\chi = \lambda = \sigma = 1$, and $M_u = M_d = M$), the subsonic and transonic formulas both predict the same wave coefficients when $M = 1$, that is, the switch from the subsonic to supersonic behavior is continuous and occurs at $M = 1$. Figure 1 shows the variation of the reflection coefficient. Subsonic relations[1] are illustrated using thin lines in the plot whereas supersonic values are shown as thick lines. It is evident that, for subsonic flow, increasing Mach number increases the reflection amplitude. As $M_{ux}$ is increased while keeping $\beta_u$ constant, $M_u$ becomes equal to one when $M_{ux} = \cos \beta_u$. For axial Mach numbers above this limit, the reflection coefficient is uniformly one for any value of $\beta_u$, as given by Eq. (2).

In the general case (curved blades, blade height change, nonzero total pressure loss), the switch from subsonic to supersonic regime involves a discontinuous change at $M_u = 1$ in the value of all three wave coefficients. Figure 2 shows the jump in transmission coefficients, for a representative set of mean flow parameters. Depending on the combination of parameters, the jumps can be significantly higher than those shown in Fig. 2.

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## Appendix 8: The Effect of Friction and Heat Transfer on Impulse in a Detonation Tube

**Reprint of:** Laviolette, J.P., Kiyanda, C.B., A.J. Higgins, "The Effect of Friction and Heat Transfer on Impulse in a Detonation Tube," Canadian Section of the Combustion Institute Spring Technical Meeting, Windsor, Ontario, May, 2002.

# The Effect of Friction and Heat Transfer on Impulse in a Detonation Tube

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## Introduction

Renewed interest in the pulse detonation engine has motivated recent investigations into the impulse generated by the detonation of a combustible mixture in an open-ended tube. Using the ballistic pendulum technique first applied by Nicholls et al. [1], recent investigations by Daniau et al. [2], Zitoun et al. [3], Cooper et al. [4], Harris et al. [5] and Tanguay et al. [6] have examined the role of ignition location, obstacles and nozzles on the impulse generated in a detonation tube. From these experiments, it has been noticed that discrepancies exist between the specific impulse measured for propane-oxygen mixtures at the three North American laboratories equipped with ballistic pendulums: McGill University, Caltech and DREV. It has also been observed that the open-ended detonation tubes used had varying aspect ratios $L/D$ between facilities, where $L$ is the length of the tube and $D$ is its diameter (see Table 1). In essence, the parameter $L/D$ represents the potential for skin friction and heat transfer losses over the total energy contained in the tube. Zitoun et al. [3] have already reported the effect of decreasing $I_{sp}$ with increasing $L/D$, but no investigations have been made to pinpoint the factor responsible.

Table 1: Volumetric Impulse versus $L/D$ for Different Facilities

| | Volumetric Impulse for Stoichiometric $C_3H_8/O_2$ (kg/m$^2$s) | Tube Aspect Ratio ($L/D$) |
|---|---|---|
| DREV [5] | 1950 | 50 |
| McGill [6] | 2100 | 33 |
| Caltech [4] | 2350 | 8 |

In the present study, a theoretical analysis aimed at approximating the magnitude of the specific impulse ($I_{sp}$) loss due to heat transfer and friction between the hot combustion products and the inner wall surface of a detonation tube is conducted for stoichiometric propane/oxygen and hydrogen/oxygen mixtures. The propagation of the detonation and the blowdown of the burned products were considered separately. The flow behind the detonation wave was modeled using the Taylor wave solution from the time of the instantaneous initiation of the detonation at the closed end up to its arrival at the open end. As for the blowdown of the combustion products, the flow was modeled as a simple wave problem and impulse loss was calculated up to the arrival of the first expansion wave at the thrust wall. Furthermore, experimental tests were conducted in order to measure the effect of varying aspect ratio $L/D$ on $I_{sp}$ for stoichiometric propane/oxygen and hydrogen/oxygen mixtures. A ballistic pendulum was used and $I_{sp}$ was obtained from the maximum amplitude of the first oscillation of the tube. Understanding the effect of friction and heat loss on the impulse generated in an open-ended detonation tube is essential for assessing the performance of pulse detonation engines.

**Theoretical Analysis**

A "zeroth order" analysis of the impulse loss due to friction is first conducted by considering only the flow at the C-J plane. The value is calculated from the definition of the friction coefficient (see Eq. 1). In Eq. 1, $D$, $L$, $V_D$, $\rho$, $u$ and $C_f$ denote the tube diameter, the tube length, the detonation velocity, the density of the gas, the velocity of the gas and the friction coefficient, respectively. Since the flow behind the detonation front is highly turbulent, $C_f$ is virtually independent of the Reynolds number and is therefore assumed constant and equal to 0.005. Since a detonation is a nearly constant volume process, $\rho$ is also assumed constant. The velocity of the flow at the C-J plane is approximately half the C-J velocity. Furthermore, it is assumed in Eq. 1 that the friction is constant and acts on the entire tube over the time the detonation takes to propagate the length of the tube. Substituting these values into Eq. 1, we can estimate the loss in impulse due to friction. Furthermore, we can obtain an expression for the actual $I_{sp}$ (see Eq. 2).

$$I_{loss} = \int_0^{L/V_D} \left(\frac{1}{2}\rho u^2\right) C_f \pi D L \, dt \qquad \text{(Eq. 1)} \qquad I_{sp} = \left(I_{sp}\right)_{ideal} - \left(\frac{V_D C_f}{2g}\right)\frac{L}{D} \qquad \text{(Eq. 2)}$$

Note from this simple analysis that we would expect $I_{sp}$ to decrease linearly with increasing tube aspect ratio $L/D$. Further, using typical values for fuel/oxygen detonations for the values of $V_D$, the loss in $I_{sp}$ is estimated to be ~30 s for $L/D$ = 50, or about 20% of the measured value for a stoichiometric propane/oxygen mixture. Because this effect is significant, and of the order of differences seen in the results in Table 1, it is therefore essential to obtain a more accurate model of the flow and also to incorporate the effect of heat loss as well.

The Taylor wave solution for the flow behind the detonation and centered rarefaction wave are used to approximate the flowfield in the detonation tube, and in turn to estimate the friction and heat loss. The heat loss and friction are not coupled into the solution of the flowfield; rather, it is assumed that heat transfer and friction do not significantly affect the flow properties. Early studies by Taylor [7] were aimed at modeling the velocity profile behind a one-dimensional detonation wave instantaneously initiated and confined to a tube. It was shown that for an isentropic expansion of the combustion products, the distribution of the gas velocity along the tube is linear behind the detonation wave. For the case of initiation at a closed end, more than 50% of the detonated gas column is at rest to satisfy the zero velocity boundary condition. Using the analysis conducted by Taylor for a perfect gas (see Figure 1), expressions for the velocity, density, temperature and speed of sound of the gas inside the unsteady expansion region are found as a function of a non-dimensional variable $\xi$ where the subscript "1" refers to the C-J properties (see Eqs. 3, 4 and 5). The variable $\xi$ represents the distance traveled by a $C^+$ characteristic line over that of the detonation front and varies from 0 to $(\gamma+1)u_1/(2V_D)$. The variables $c$ and $\gamma$ are the sound speed and the perfect gas constant respectively. The value for $\gamma$ and the C-J properties are obtained from the CEA NASA code.

The flow inside the detonation tube during the blowdown of the combustion products is modeled using the solution of the one-dimensional simple wave problem of a centered rarefaction fan at the open end of the tube propagating into quiescent gas (see Figure 2).

$$u(\xi)=\frac{2V_D}{(\gamma+1)}\xi \qquad \text{(Eq. 3)}$$

$$\rho(\xi)=\rho_1\left[(u(\xi)-u_1)\frac{(\gamma-1)}{2c_1}+1\right]^{2/(\gamma-1)} \qquad \text{(Eq. 4)}$$

$$\left(\frac{c(\xi)}{c_1}\right)^2=\frac{T(\xi)}{T_1}=\left(\frac{\rho(\xi)}{\rho_1}\right)^{\gamma-1} \qquad \text{(Eq. 5)}$$

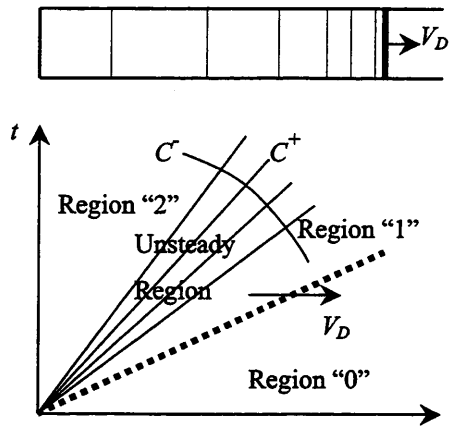

Figure 1: Taylor Wave

The properties of the expanding gas are thus obtained (see Eqs. 6, 7 and 8), the moving portion of the Taylor wave being neglected. The perfect gas properties inside the tube are given by the Taylor solution for the gas brought to rest by the expansion fan (subscript '2' below). These can be found by substituting $u(\xi)=0$ in the above equations.

$$u(x,t)=\frac{2}{(\gamma+1)}\left(c_2+\frac{x}{t}\right) \qquad \text{(Eq. 6)}$$

$$\rho(x,t)=\rho_2\left[1-\frac{(\gamma-1)}{(\gamma+1)}\left(1+\frac{x}{tc_2}\right)\right]^{2/(\gamma-1)} \qquad \text{(Eq. 7)}$$

$$\left(\frac{c(x,t)}{c_2}\right)^2=\frac{T(x,t)}{T_2}=\left(\frac{\rho(x,t)}{\rho_2}\right)^{\gamma-1} \qquad \text{(Eq. 8)}$$

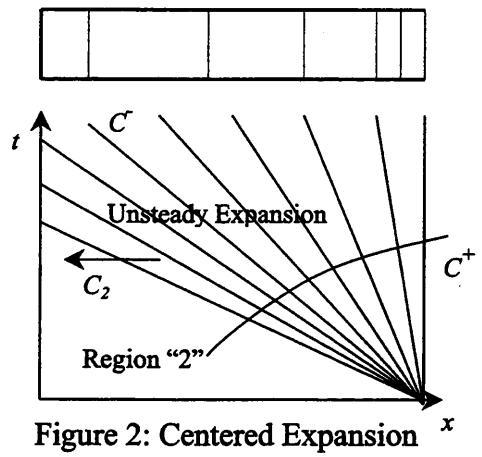

Figure 2: Centered Expansion

The loss of $I_{sp}$ for both effects is calculated up to the arrival of the first expansion wave at the closed end of the tube. Since Harris et al. [5] has shown that 75% of the total $I_{sp}$ generated has been delivered by that time, the present model should capture most of the main features of the flowfield responsible for impulse loss.

The magnitude of the effect of friction on $I_{sp}$ is calculated from the definition of the friction coefficient (see Eq. 9). On the other hand, the impulse loss due to heat transfer is determined from the expressions used by Edwards et al. [8] and also Sichel et al. [9] to evaluate the heat loss behind a detonation wave. The equations from which the $I_{sp}$ losses can be obtained are shown below:

$$I_{sp\ friction}=\frac{\int_0^t\int_0^\beta\left(\frac{1}{2}\rho u^2\right)C_f\,\pi D\,dx\,dt}{M_R\,g} \qquad \text{(Eq. 9)}$$

$$Q_{Edwards} = \int_0^t \int_0^\beta C_f C_p u (T_0 - T_w) \pi \frac{D}{2} \rho \, dx \, dt \qquad \text{(Eq. 10)}$$

$$Q_{Sichel} = \int_0^t \int_0^\beta \frac{\tau_w C_p (T_0 - T_w)}{u \, \mathrm{Pr}^{2/3}} \pi D \, dx \, dt \qquad \text{(Eq. 11)}$$

Equations 10 and 11 both make use of Reynolds analogy and give a value for the heat loss from the hot combustion products to the inner wall boundary following a detonation wave in Joules. β is the upper bound of the integral and Pr is the Prandtl number taken as 0.815, which is the same value used by Sichel et al. [9]. Furthermore, $\tau_w$ is the shear stress at the wall, $M_R$ is the mass of the reactants and $C_p$ is the specific heat at constant pressure, which is obtained from perfect gas relations and assumed constant. The results of Equations 10 and 11 are expressed as the ratio of the heat transfer out of the tube over the total heat released by the detonation wave. This last value is calculated from the difference of the enthalpies of formation between the products of combustion and the reactants. In order to relate a change in the effective heat release to a change in specific impulse, we must consider how heat release is converted into impulse. Since $I_{sp}$ is related to the square root of the heat released, a small percent increase in heat release results in half the same percent of increase in $I_{sp}$ (see Eq. 12).

$$\frac{\Delta Q}{Q} = 2 \frac{\Delta I_{sp}}{I_{sp}} \qquad \text{(Eq. 12)}$$

One must realize that the aim of this paper is to assess the order of magnitude of the impulse loss due to friction and heat transfer. It is not intended to quantify the impulse losses with high accuracy. Moreover, more confidence is given to the friction values since they originated from a definition, the authors would think that the heat loss values are much less certain.

**Experimental Setup**

The experimental setup consisted of a stainless steel detonation tube with varying length of 1.24, 2.11 and 3.34 m and a constant 6.35 cm inner diameter. The smooth wall tube had one end closed while the open end was sealed with a 0.025-mm Mylar diaphragm. Prior to each test, the tube was evacuated and then filled with a stoichiometric propane/oxygen or hydrogen/oxygen mixture by means of calibrated choked orifices. The tube was filled to one atmosphere and then flushed for 10 tube volumes in order to ensure mixture uniformity. The tube was equipped with 10 ports along its length to accommodate pressure transducers and/or ionization probes to measure the leading shock and combustion front velocity. The combustible mixture was ignited from the closed end using a weak spark and DDT occurred within the first diameters of the tube. The motion of the tube was monitored by a video camera, which was then used to determine the total impulse generated. Further details can be found in [6]. The tests involved varying the aspect ratio of the tube and measuring the specific impulse. It was possible to measure the $I_{sp}$ for *L/D*'s of 19.45, 33.23 and 52.6.

## Results and Discussion

The results from the experiments for stoichiometric propane/oxygen and hydrogen/oxygen mixtures are shown in Fig. 3 and 4 respectively. The experimental data is plotted along with the theoretical $I_{sp}$ obtained from the subtraction of the various calculated impulse loss values from an ideal $I_{sp}$. This ideal $I_{sp}$ was obtained using the analytical model derived by Wintenberger et al. [10]. Looking at Fig. 3 for propane/oxygen, it is noticed that friction alone cannot account for the impulse deficit with increasing *L/D* since the *Ideal $I_{sp}$–Friction* curve does not follow the experimental trend. It is further observed that the theoretical $I_{sp}$ curves, which incorporate both friction and heat transfer losses by the Sichel or Edwards model, show behaviors that more closely follow the experimental trends. Experimental data shows a 9.1% decrease in $I_{sp}$ over the tested range of *L/D* compared to 12.3% and 11.3% for the results taking into account friction and heat losses using Sichel's and Edwards' model respectively. Friction alone is responsible for 4.5% loss of $I_{sp}$, which is half that for heat loss over the experimental range of *L/D*. Therefore, it seems that heat loss is the dominant factor over friction that affects the final $I_{sp}$ generated in a detonation tube.

Examining Fig. 4 for hydrogen/oxygen, it is seen that the $I_{sp}$ loss due to friction is again too small to account for the actual drop with aspect ratio *L/D*. The experimental data shows the $I_{sp}$ decreases by 22%, while the friction is only responsible for a 4.6% decrease according to theoretical calculations for the same *L/D* range. It is also observed that the theoretical $I_{sp}$ curves, which take into account heat and friction losses, fit the experimental trend better than the one that considers only friction. Combined heat loss and friction effects results in a 12.2% and 11.2% decrease using Sichel's and Edwards' respectively over the experimental range of *L/D*. Thus, it is again seen that friction alone does not explain the reduction of $I_{sp}$ with increasing *L/D*. It seems that heat loss to the tube wall is the main factor.

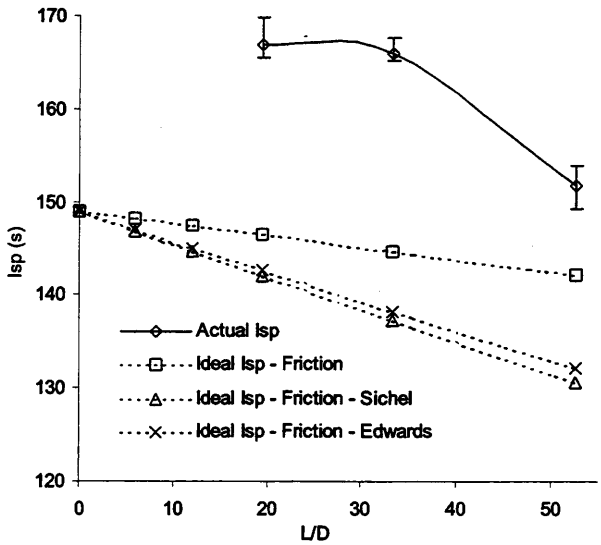


Figure 3: $I_{sp}$ vs. *L/D* for Propane/Oxygen

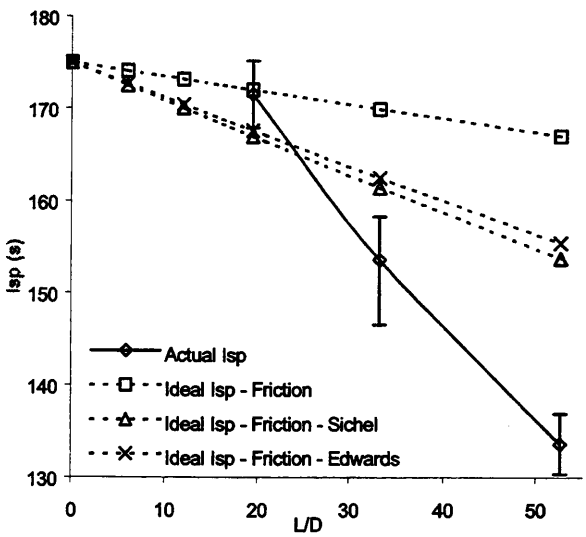


Figure 4: $I_{sp}$ vs. *L/D* for Hydrogen/Oxygen

## Conclusion

The results of this investigation clearly demonstrate that friction and heat transfer are a dominant effect on the impulse generated in an open-ended detonation tube. Simple dimensional

reasoning suggests that friction losses should result in specific impulse decreasing linearly with increasing tube aspect ratio. A trend which is observed in the present experiments and in other facilities equipped with ballistic pendulums (Zitoun et al. [3], Cooper et al. [4], Harris et al. [5] and Tanguay et al. [6]). A more refined estimate of the losses in impulse due to friction and heat transfer to the tube walls predicts losses on the order of 10-15% of the $I_{sp}$ for tube aspect ratios in the range of 20 to 50, in quantitative agreement with the actual decrease in impulse observed as tube aspect ratio is increased to these values. This analysis also suggests that heat transfer is also the dominant effect, responsible for almost an order of magnitude greater loss in $I_{sp}$ than friction.

While the present analysis uses simple, analytic models of the flowfields involved under the assumption of a calorically perfect gas, it is possible to extend this analysis to include more realistic flowfield models with variable specific heats as determined by equilibrium calculations and to couple the effect of friction and heat transfer to the flowfield solutions. While such a model will result in more quantitatively accurate solutions, it will not change the conclusion that heat transfer and friction are "first order" considerations in determining the impulse generated by pulse detonation engines. Since the losses in impulse observed here (10-30%) are of the same order as the hypothetical increase in $I_{sp}$ obtained by using a constant volume combustion cycle (Bussing et al. [11]), the effect of heat transfer and friction warrant further attention.

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The initiation of detonation in hydrocarbon fuel-air mixtures and the effect initiation has on performance are two key issues for the assessment and progress of Pulse Detonation Engines. This report presents the results of experimental studies into the initiation of detonation and the impact of initiation on the impulse generated in a single-cycle Pulse Detonation Engine. In order to facilitate the prompt initiation of detonation, a number of chemical sensitizers were considered (nitrates, nitrogen dioxide, peroxides). None of these were shown to have a significant sensitizing effect, as quantified either by the run-up distance to detonation or by the detonation veil size. Partial reforming of the fuel/oxygen mixture via the "cool flame" process was shown to have a significant sensitizing effect, reducing the run-up distance by a factor of two and the cell size by a factor of three. This effect was transient, in that it was only observed immediately prior to the onset of cool flame. The ability to initiate an unsensitized fuel-air mixture via a turbulent jet of combustion products was demonstrated in two different facilities at different scales. Different techniques of creating a nearly instantaneous constant volume explosion in a pre-combustion chamber were investigated. These techniques were then used to drive a turbulent jet of combustion products through orifices of different geometries. The use of flame tubes was shown to be highly effective in creating constant volume explosion pressures, and the use of an annular orifice to create a centrally focused jet was found to be the most effective orifice design. The scaling for jet initiation of detonation was determined in terms of the characteristic cell size.

The role of initiation in the impulse generated by a single cycle of a Pulse Detonation engine was also investigated using a ballistic pendulum. It was shown that, over a wide range of equivalence ratios, the impulse generated by direct initiation of detonation was the same as that generated by deflagration to detonation transition. Initiation at the open vs. the closed end of the tube was also shown to give comparable impulse. The friction and heat losses to the tube were shown to have a significant effect on impulse, which become dominant as the tube aspect ratio (length to diameter ratio) increased to large values.

The results of this study did not identify a chemical additive that is a significant sensitizer to detonation. Reforming the fuel via cool flame was shown to have a significant effect, but how this technique would be implemented in an engine remains unresolved. An intense jet of combustion products is capable of initiating detonation in a fuel/air mixture, provided the jet diameter is sufficiently large. The impulse measurement results show that initiation of detonation may not be necessary if the combustible mixture can still be burned quickly enough via fast turbulent flame. The effect of heat transfer and friction must be carefully considered in interpreting impulse measurement.

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